THE UNIVERSITY OF ALBERTA

GAMMA RADIOLYSIS OF LIQUID CYCLOPENTANE

by

AJIT SINGH

M.Sc.

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

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The undersigned certify that they have read and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled " GAMMA RADIOLYSIS OF LIQUID CYCLOHEXANONE", submitted by AJIT SINGH in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Ring cleavage has been found to be more important in the gamma radiolysis of liquid cyclohexanone than that found in cyclohexane by other workers. The ratio of ring opening to C-H bond split in cyclohexanone is about ten times greater than that in cyclohexane.

The G values of the major products are; hydrogen (0.76), carbon monoxide (0.48), 1-pentene (0.22), 5-hexenal(0.85), cyclohexenone (0.4), cyclohexanol (0.5), total dimer (1.15) and polymer (1.8 cyclohexanone units). A large number of minor products have also been measured.

Benzene inhibits the formation of hydrogen and the dimers, and sensitizes the formation of carbon monoxide, 1-pentene and 5-hexenal, during the radiolysis of cyclohexanone. Ethylene and cyclohexanol seem to be unaffected by it. Activation transfer type processes are most likely involved in the inhibition and sensitization by benzene.

Except for its lack of effect on the radiolytic formation of ethylene, the behaviour of 2,3-dimethyl-1,3-butadiene is in sharp contrast to that of benzene. It is marked by faster inhibition of products in general and lack of sensitization of any product.

The formation of products has been considered in terms of some of the more probable mechanisms. Hydrogen formation seems to involve complex processes. The formation of other products is consistent with free radical mechanisms.

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I. INTRODUCTION

A. General.

Radiation chemistry has been defined [Lind et al, 1961] as "the science of the chemical effects brought about by the absorption of ionizing radiations in matter." Radiation chemical processes are at least as old as the Universe, in as much as both matter and ionizing radiations have been integral parts of it. However, the known serious efforts of scientists towards the understanding of these processes date back only to the beginning of this century.

Roentgen in announcing his discovery of X-rays is reported [Lind et al, 1961] to have pointed out the similarity between their chemical effects and the chemical effects of light on the silver salts of a photographic plate. Becquerel discovered radioactivity in 1896 [see Lind et al, 1961] and later showed that β-and X-rays can produce many of the reactions that can be brought about by light, such as the change of white to red phosphorous.

The names of various scientists are connected with the suggestion that the α- particle induced reactions might be directly proportional to the number of ions initially generated [e.g.Bragg, Curie, and LeBlanc; see Lind, 1928 and Dainton, 1958]. This suggestion, coupled with the convenience of measurement of the number of ions produced by α-particles in gas phase led to the concept of ionic yield, $M/_N$ (number of molecules reacted, M, divided by the number of ions formed, N). However, the fact that the energy

expended by α - particles in creating an ion pair in air exceeded, by a factor of about two, the ionization potential of either oxygen or nitrogen indicated that processes other than simple ionization are involved. In 1936 Eyring and coworkers [Eyring et al, 1936] examined theoretically the α- particle induced ortho-para conversion of hydrogen and concluded that reactions involving free radicals were important in this system. A similar conclusion was reached by Hirschfelder and Taylor [Hirschfelder and Taylor, 1938] who extended the method to the radiolysis of CO, O_2, CO_2 and their mixtures. Thus the growing importance of free radical reactions together with the fact that ions could not be measured in the liquid phase led to the discontinuance of the use of ionic yield, M/N, and the radiolytic yields are now expressed as G values i.e. the number of molecules formed or destroyed per 100 ev of energy absorbed by the system.

B. Physical and Chemical Effects of γ - Rays.

1. Interaction of γ- rays with the system.

Gamma rays impart energy to a system mainly by three processes as follows [see Hine and Brownell, 1956].

a. Photoelectric effect.

In this process the γ- photon is entirely absorbed by the medium, with the ejection of a fast electron. This process is mainly important for γ- radiations of low energy ($h\nu < 0.1$ Mev) and for atoms of high atomic number.

b. Pair production.

The γ - photon can interact with the nucleus of an atom to produce an electron - positron pair. The process can occur with γ - rays of energy $\geqslant 1.02$ Mev and is unimportant for energies less than about 5 Mev.

c. Compton effect.

In this process the γ - rays lose part of their energy to the electrons of the system by collisions. These energetically ejected electrons (primary electrons) in turn dissipate their energy in the medium causing ionizations and excitations. It has been estimated that for 1 Mev photons the energy of these primary electrons (also called Compton electrons) varies up to about 0.8 Mev, having a mean value of 0.45 Mev [see Kuppermann, 1959]. The Compton effect is the main energy dissipation process when Co^{60} γ - rays (1.17 and 1.33 Mev) interact with water, or with organic systems.

2. Events immediately following the absorption of energy by the system.

The overall process which starts with the passage of high energy radiations through a system and leads to the ultimate formation of products can be broadly divided into three stages as follows [see Kuppermann, 1959].

a. Physical stage.

This stage consists of the dissipation of energy in the system and its duration is $\sim 10^{-15}$ sec. An electron with a few Mev energy would dissipate energy over a small portion of its track ($\sim$ 100 A^{o}), in the system, in $\sim 10^{-18}$ sec and a secondary electron with low energy ($\sim$ 100 ev) will dissipate its energy in $\sim 10^{-16}$ sec. The absorption of energy in matter is thus a very fast phenomenon and is essentially completed before any chemical change in the medium has time to occur. It gives rise to a large number of excited molecules and ions, in a highly non-uniform spatial arrangement.

b. Physicochemical stage.

This is the stage in which the excited molecules and ions formed in the physical stage reach internal thermal equilibrium. It lasts for $\sim 10^{-12}$ sec, i.e. of the order of magnitude of molecular vibration times, during which internal molecular rearrangements can take place. During this stage excited molecules and ions dissipate their excess energy by bond rupture, internal conversion, energy transfer to neighbouring molecules etc.

c. Chemical stage.

During this stage the chemically reactive species produced in the physicochemical stage undergo chemical reactions, and it extends beyond $\sim 10^{-11}$ sec and may take much longer (sec or hours) depending upon the conditions of radiolysis.

3. Magnitude of energy of the excited species.

The usefulness of knowing the energy states of the excited species, involved in radiolytic systems, can hardly be overemphasized. However, knowledge on the matter is extremely limited, making it difficult to decide on the correctness of various views that have been put forward on the subject. Some of these views are mentioned below.

One of the suggestions has been [Burton et al, 1952] that the excited species produced in a system are, for the most part, in their lowest excited state. Theoretical calculations for benzene [Inokuti, 1958] show that the cross section for excitation of π-electrons by fast electrons to the lowest excited levels is very large. On the other hand it has been stressed [Platzman, 1962] that the typical molecular excitation in radiolysis lies very high. The results of a quantitative treatment for excitation and ionization of helium by high energy radiations is reported [Platzman, 1961] to show that the

number of excitations to the lowest excited states is only $\sim$ 1% of the total number of excitations. This view receives support from the work of Oster and Kallman [Oster and Kallman, 1962] who have shown by a study of the energy transfer from benzene to carbon tetrachloride, in their binary solutions, that in the case of excitation by ionizing radiations, the excited states of benzene higher than the excited singlet at 254 $m\mu$ ($\sim$ 5 ev) are predominantly involved.

a. Fano's concept of collective excitation.

Fano considers that the energy spectrum of primary excitations produced by high energy radiations differs substantially in the condensed and the gaseous state of matter, the excitations being shifted towards higher energy in the condensed state [Fano, 1960]. He draws the following conclusion from the energy - loss spectrum of electrons in solid films.

" The peak (at $\sim$ 18 ev) in such a loss spectrum is understood to correspond to a collective excitation involving the electrons of a rather large volume of matter, perhaps 100Å or more in diameter. This excitation lasts, in its initial form, only for a very short time of perhaps $\sim 10^{-15}$ sec."

It must be pointed out that various features of collective excitation and its importance in radiation chemistry are not clear e.g. whether the excitation is really spread over a large region (diameter $\sim$ 100Å) or is it merely that the exact location of the excitation within this region cannot be determined. Fano himself has pointed out " It is not known how it (initial collective excitation) evolves, e.g., whether it spreads out, or whether it becomes quickly localized within a single atom or group of atoms thus becoming similar to the excitation produced in gaseous matter. Thus it cannot be said at this time whether the initial

collective aspect of the excitation, which had been overlooked in the past, has actually a significant influence on its eventual physico-chemical effects."

If upon further clarification and understanding, the application of this concept to radiation chemistry is accepted, it might provide alternate explanations for some effects. For example, primary recombination of radicals due to the cage effect has been invoked to explain some of the radiolytic differences between the liquid phase and the gaseous phase [Jones et al, 1958]. An alternate explanation might be reduced primary dissociation in the liquid phase due to the spreading out of the energy without chemical change subsequent to collective excitation by high energy radiations.

b. <u>Superexcited states.</u>

Platzman [Platzman, 1962, 1963] has drawn attention to the high lying, electronically excited states of neutral atoms and molecules having excitation energy E greater than the lowest ionization energy I. He points out that in these molecules, where $E > I$ ionization is not inevitable. He calls an excited state with energy $E > I$ a "superexcited" state, and such states are suggested to play an important role in the radiation chemistry of gases, and perhaps also in the radiation chemistry of condensed phases.

Platzman goes on to suggest that superexcited molecules could break up into atoms or radicals, at least one of which is electronically excited. Thus it is deemed possible that excited hydrogen atoms, which possess a minimum excitation energy of 10 ev, are common products in the dissociation of superexcited states of the simple hydrides, e.g. water, and of organic compounds. In support of this suggestion is the observation of atomic hydrogen emission lines [Horie et al, 1957]

when molecules containing hydrogen (e.g., H_2O, CH_3OH) are irradiated with fast electrons. It is further suggested that reactions of such energetic H atoms may be responsible for some of the "molecular" yields of hydrogen in various systems. Other possible reactions for these energetic hydrogen atoms have also been suggested.

4. Reactions of the excited species.

The main action of high energy radiation in a system is to cause electronic excitation and ionization. The excited and ionized species so formed can give products (i) directly by dissociation or rearrangement, (ii) by reaction with the surrounding molecules or (iii) by producing more stable but still highly reactive species e.g. free radicals. The scope of these processes is briefly illustrated here.

a. Ions.

Positive ions are formed by the ejection of electrons from molecules. Since the ions are electron deficient, they possess the properties of free radicals as well.

Though a lot of information has been obtained on the dissociation of positive ions by mass spectrometric studies, the usefulness of such information for interpretation of radiolytic reactions is limited. Mass spectrometric studies are usually carried out under conditions where the ions formed do not undergo any collisions and $\sim 10^{-5}$ sec elapse between the formation of the parent ions and the final collection of all the ions [Lampe et al, 1961; Swallow, 1960]. However, in gaseous systems at atmospheric pressures a molecule collides $\sim 10^{9}$ times per second. If the positive ions formed by radiolysis do not undergo unimolecular decomposition in times $< 10^{-9}$ sec, they would be vulnerable to

bimolecular processes of energy transfer and reaction. In the condensed phase the bimolecular processes are likely to intervene in even shorter time.

Increasing consideration is being given to reactions between ions and molecules in the interpretation of radiolytic processes. It has been pointed out [Stevenson, 1957] that in gas phase radiolysis, ion-molecule reactions would compete effectively with ion-neutralization. Schaeffer and Thomson [Schaeffer and Thomson, 1959] have found that ion-molecule reactions are necessary to explain the rate of exchange of hydrogen and deuterium induced by high energy radiations. The H_2^+ ions formed upon irradiation are rapidly converted into H_3^+ by the reaction I.1.

$$H_2^+ + H_2 \longrightarrow H_3^+ + H \text{ ---------------------------------- (I.1)}$$

The H_3^+ then transfers a proton to deuterium(reaction I.2) and acts as a chain carrier to cause the exchange.

$$H_3^+ + D_2 \longrightarrow H_2 + HD_2^+ \text{ --------------------------- (I.2)}$$

The importance of ions in this reaction is rather dramatically shown by Schaeffer and Thomson [Schaeffer and Thomson, 1958]. They found that while Kr and Xe had no effect on the thermal and photolytic H-D exchange, these gases, in small amounts, practically stopped the radiolytic exchange. They concluded that atom-induced reaction chains were insignificant as compared to ion induced chains. They suggested that Xe and Kr acted by charge exchange, both having lower ionization potentials than H^+, H_2^+ or H_3^+.

Ion-molecule reactions have been invoked [Miesels et al, 1957] to explain the radiolysis of methane admixed with argon and krypton, and provide examples of ion-molecule condensation and loss of molecular

hydrogen. For example,

$$CH_3^+ \quad + \quad CH_4 \longrightarrow \quad C_2H_7^{\cdot\,*} \quad \text{----------------------} \quad (I.3)$$

$$C_2H_7^{+\,*} \longrightarrow C_2H_5^+ \quad + \quad H_2 \quad \text{----------------------} \quad (I.4)$$

Ion-molecule condensation has also been postulated by Wagner [Wagner, 1961] to explain the formation of dimeric products in the radiolysis of liquid propylene, the reaction scheme being

$$(C_3H_6)^+ \quad + \quad C_3H_6 \longrightarrow [(C_3H_6)^+ \underset{H^-}{\text{----}} (C_3H_6)] \longrightarrow$$

$$\longrightarrow (C_6H_{12})^+ \quad + \quad e^- \longrightarrow (C_6H_{12})^* \longrightarrow C_6H_{12} \quad \text{-----} (I.5)$$

the scheme also providing an example of hydride ion transfer.

Another example of hydride ion transfer is provided by Futrell [Futrell, 1959] who has suggested that a key reaction in the radiolysis of (gaseous and liquid) n-hexane was a hydride ion transfer.

$$R^+ \quad + \quad C_6H_{14} \longrightarrow C_6H_{13}^+ \quad + \quad RH \quad \text{----------------} \quad (I.6)$$

Convincing proof of the role of ion-molecule reactions in radiolysis has been provided [Collinson et al, 1959] by investigation of the low temperature radiolytic polymerization of isobutene. They showed that the polymerization is due to ionic propagation and tertiary butyl carbonium ion was suggested as the most likely initiator. Attempts to polymerize isobutene at -78°C with free radicals from the photolysis of diacetyl, benzoin and benzil were unsuccessful. Isobutene irradiated with γ- rays in the pure state was consumed with $G = (3.7 \pm 1.2)\ 10^2$.

Knowledge about the role of negative ions in radiation chemistry is much more limited. Their possible role has been speculated upon by Burton and Lipsky [Burton and Lipsky, 1957] and also by Rao and coworkers [Rao et al, 1962] who have also reported the formation of negative ions in gamma irradiated organic glasses at $-196^{\circ}C$.

b. Excited molecules.

There are two ways in which excited molecules can be formed. One is from the neutralization of a positive ion by an electron or a negative ion, giving a molecule in a highly excited state. The other is direct excitation by the high energy radiations.

Excited molecules are subject to deactivation by energy loss and those that are not deactivated may decompose into free radicals and molecular products.

(i) Free radicals.

The bulk of the knowledge about free radicals is derived from pyrolytic and photochemical studies [see Steacie, 1954]. Typical reactions of free radicals, illustrated using the cyclohexyl radical as an example, are abstraction,

$$\cdot(C_6H_{11}) + RH \longrightarrow C_6H_{12} + R \qquad \text{(I.7)}$$

addition to double bonds,

$$\cdot(C_6H_{11}) + RCH = CHR \longrightarrow C_6H_{11} - CHR - \dot{C}HR \qquad \text{(I.8)}$$

radical combination,

$$\cdot(C_6H_{11}) + \cdot(C_6H_{11}) \longrightarrow C_6H_{11} - C_6H_{11} \qquad \text{(I.9)}$$

and disproportionation.

$$\cdot(C_6H_{11}) + \cdot(C_6H_{11}) \longrightarrow C_6H_{12} + C_6H_{10} \qquad \text{(I.10)}$$

In recent years various workers have devoted studies to the elucidation of the role of free radicals in radiolytic systems, as

briefly described below.

Halogens, hydrogen halides, the free radical 1,1' - diphenyl-2-picrylhydrazyl and the monomer (styrene) polymerization technique have been used by various workers for the detection of free radicals in the radiolysis of organic systems [Schuler, 1958]. Adams and coworkers [Adams et al, 1959] determined radical yields (and molecular yields) in the γ- radiolysis of some saturated organic liquids by using ferric chloride and benzoquinone as free radical scavengers. They found $G(H) > 2$ and $G(R.) > 6$ for primary and secondary alcohols. It may be pointed out, however, that reduction by H atoms may not be distinguishable from reduction by electrons [Rao et al, 1962].

Holroyd and Klein [Holroyd and Klein,1962] have used labeled ethyl radicals as scavengers. These were generated by addition of the hydrogen atoms produced in the system to $C_2{}^{14}H_4$ that had been added to the system. At the high dose rates employed, the $C_2{}^{14}H_5$ radicals combined with the radical intermediates of the radiolysis of the hydrocarbon thus forming labeled products. They have related the yields of these labeled products to the yields of the radicals produced and thus obtained individual radical yields in the radiolysis of n-pentane, n-hexane and n-heptane.

Dorfman has briefly reviewed [Dorfman, 1961] the work done by various workers on the detection of free radicals using the Electron Spin Resonance technique and has cited the following among the radicals that have been detected; allyl (radiolysis of cyclopropane), cyclopentyl (radiolysis of cyclopentane), and cyclohexyl (radiolysis of cyclohexane). Ohnishi and coworkers [Ohnishi et al, 1962] have used the E.S.R. technique to study the free radicals produced in benzene and related hydrocarbons, by irradiation at - 196°C. They have identified the following radicals

cyclohexadienyl (C_6H_7) and phenyl from benzene, cyclohexyl from cyclohexane, and predominantly cyclohexyl from the benzene + cyclohexane mixture.

(ii) Molecular products.

The formation of molecular products might be illustrated by the formation of cyclohexene and hydrogen from excited cyclohexane.

$$C_6H_{12}^{*} \longrightarrow C_6H_{10} + H_2 \quad \text{--------------------------} \quad (I.11)$$

There has been considerable discussion about the formation of molecular products. Hardwick has reflected upon this, "The 'molecular' process (or processes), as it is defined experimentally, is a process which is not affected by the presence of small amounts ($<2\%$) of highly reactive materials, particularly free radical scavengers. It is generally considered not to involve freely diffusing free radicals. Since by its very nature one is presented with a fait accompli, direct investigation by modifying such a process by various means cannot be made. One can argue only by inference and by analogy " [Hardwick, 1962]. He then goes on to discuss various alternate mechanisms which would give the same observed results, e.g. abstraction by hot hydrogen atoms. Dyne and Jenkinson [Dyne and Jenkinson, 1962] have studied the isotopic composition of radiolytic hydrogen evolved from mixtures of benzene and cyclohexane with their deuterated analogues and conclude that true molecular detachment (reaction I.11) does occur in the system studied.

C. Previous work on ketones.

1. Cyclopentanone.

The radiolysis of cyclopentanone by CO^{60} γ - rays has been studied by Katayama and coworkers [Katayama et al, 1962]. They compared their results with the previously obtained results of photolysis

[Benson and Kistiakowsky, 1942; Blacet and Miller, 1957; Srinivasan, 1961], as follows:

a. Liquid and gas phase photolysis at 3130Å produces 4- pentenal. None has been observed either in gas or liquid phase radiolysis.

b. No free radicals are detectable in the gas phase photolysis. They suggest that free radicals are present in the radiolysis.

c. Cyclobutane is a major product of photolysis but is not a significant product of radiolysis.

d. No hydrogen is present in the photolysis at 3130Å, but hydrogen is a major product in radiolysis.

e. An oil is formed and has been characterized in the radiolysis but slight formation of polymer has only been indicated in photolysis without characterization.

It may be pointed out that Blacet and Miller [Blacet and Miller, 1957] postulated the presence of free radicals (biradicals) to explain their results. Also, the characterization of the oil (radiolysis product) by Katayama and coworkers seems to be rather cursory [Katayama et al, 1962] and no effort seems to have been made to detect the presence of 'dimers' that are presumably formed, and might be present in the oil.

They have found the major products of radiolysis of liquid cyclopentanone to be CO ($G \sim 1.5$), H_2 ($G = 0.67 \pm 0.05$), C_2H_4 ($G \sim 0.3$) and an oil (mol wt ~ 200, $G \sim 1$). The hydrogen yield was independent of dose and temperature (100° vs 25°). The yields of both CO and C_2H_4 increased with temperature.

They observed that the prior addition of oxygen, iodine, or cyclohexene to the ketone reduced the radiolytic yields of C_2H_4 and H_2

but slightly increased the radiolytic yield of CO. Further, radiolysis of cyclopentanone vapour was found to give, qualitatively, the same major gaseous products as obtained in the liquid phase.

2. Acetone

The radiolysis of acetone has been the subject of several investigations. McLennan and Patrick studied the effect of high speed electrons on the vapour of various organic compounds including acetone [McLennan and Patrick, 1931]. Ausloos and Paulson studied the liquid and vapour phase radiolysis of acetone [Ausloos and Paulson, 1958], and were able to explain the formation of most of the products on the basis of free radical reactions. The three primary processes, suggested, are

$$CH_3COCH_3 \rightsquigarrow 2CH_3 + CO \quad \text{------------} \quad (I.12)$$

$$\rightsquigarrow CH_3\dot{C}O + CH_3 \quad \text{------------} \quad (I.13)$$

$$\rightsquigarrow H + \cdot CH_2COCH_3 \quad \text{------------} \quad (I.14)$$

They pointed out that the yield of CO was almost independent of temperature ($-80^{\circ}C$ to $27^{\circ}C$) so that it served as a measure of reaction I.12. In a later study [Ausloos, 1961] it was found that addition of cyclohexane to acetone, prior to radiolysis, decreased the yield of CO. This decrease was attributed to the radical scavenging action of CO. The decrease in the radiolytic yield of CO from the solutions of cyclohexane in acetone did not occur if DPPH was also present in the solution. This was interpreted as due to more efficient scavenging of the free radicals by DPPH than by CO. In a low temperature radiolysis ($-195^{\circ}C$) [Ausloos,1961] of a1:1 mixture of CH_3COCH_3 and CD_3COCD_3, the following scavenging actions were attributed to CO.

$CH_3 + CO \longrightarrow CH_3\dot{C}O$ -------------------- (I.15)

$CD_3 + CO \longrightarrow CD_3\dot{C}O$ -------------------- (I.16)

$H + CO \longrightarrow H\dot{C}O$ -------------------- (I.17)

$D + CO \longrightarrow D\dot{C}O$ -------------------- (I.18)

It had been postulated [Ausloos and Paulson, 1958] that "hot" hydrogen atoms may be formed in reaction, I.14. Ausloos [Ausloos, 1961] has suggested that since the value of the HD/D_2 ratio increases only slightly upon addition of benzene to a 1:1 mixture of CH_3COCH_3 and CD_3COCD_3 "hot" hydrogen atoms must be adding on to benzene rather than abstracting an H atom from it. However, Barker studied the effect of dose rate and LET on the radiolysis of liquid acetone [Barker, 1961] and found this suggestion in conflict with his results. He has explained the dependence of hydrogen yield on LET by a hydrogen atom recombination process in the spurs. He also found that G(CO) decreased with increasing dose rate, and indicates that this may be due to some radical scavenging action of CO.

In a later study Barker has investigated the γ- radiolysis of liquid acetone over a wide dose range with an effort at the measurement of all the products formed [Barker, 1963]. He suggests that the results obtained can be interpreted using free radical reactions only and that the majority of the important products can be formed following the primary decompositions (reactions I.12 to I. 14). Exceptions were isopropyl alcohol, acetic acid and other minor gaseous products. The mode of formation of acetic acid has not been suggested and the formation of isopropyl alcohol has been postulated as follows:

$CH_3COCH_3^* + CH_3COCH_3 \longrightarrow CH_3\dot{C}OHCH_3 + \cdot CH_2COCH_3$ -------(I.19)

$H + CH_3\dot{C}OHCH_3 \longrightarrow CH_3CHOHCH_3$ --------------------------(I.20)

Acetic acid has also been observed as a product of radiolysis of liquid acetone by Drienovsky who assumes that ketene is first formed which reacts with water to form acetic acid [Drienovsky, 1962]. He presumes that water is formed along with the condensation products of acetone. In addition to studying the dimeric and condensation products of the radiolysis of acetone, semiquantitatively, he also studied the radiolytic formation of acids and formaldehyde from the ketone in the presence of oxygen and hydrogen. The G values for acetic acid and formaldehyde were found to be greater in the presence of oxygen (1.95 and 6.3 respectively) than in the presence of hydrogen (0.71 and 2.8 respectively).

Barker also studied the effect of added iodine in the radiolysis of acetone [Barker, 1963] and found that the yield of methane decreased by 76% [compare $\backsim$ 85% decrease at slightly higher iodine concentration; Ausloos and Paulson, 1958] while $G(H_2)$ and G(CO) seemed to be relatively unaffected. He found G(consumption) of iodine atoms to be 4.1 and has compared it with the results of earlier workers; G(consumption) of Fe^{+++}= 11.8 and G(consumption) of DPPH = 7.5 [see Barker, 1963; ref 15 and 16]. He mentioned the uncertainty in the determination of his value due to slow reaction (without irradiation) of iodine and acetone.

Barker used P_2O_5 to dry the acetone [Barker, 1963]. He has also given results from a few samples using acetone that was not dried. The yields of most of the products show significant differences and he attributes at least part of the differences in results to the presence of trace quantities of water. It may be pointed out, however, that P_2O_5

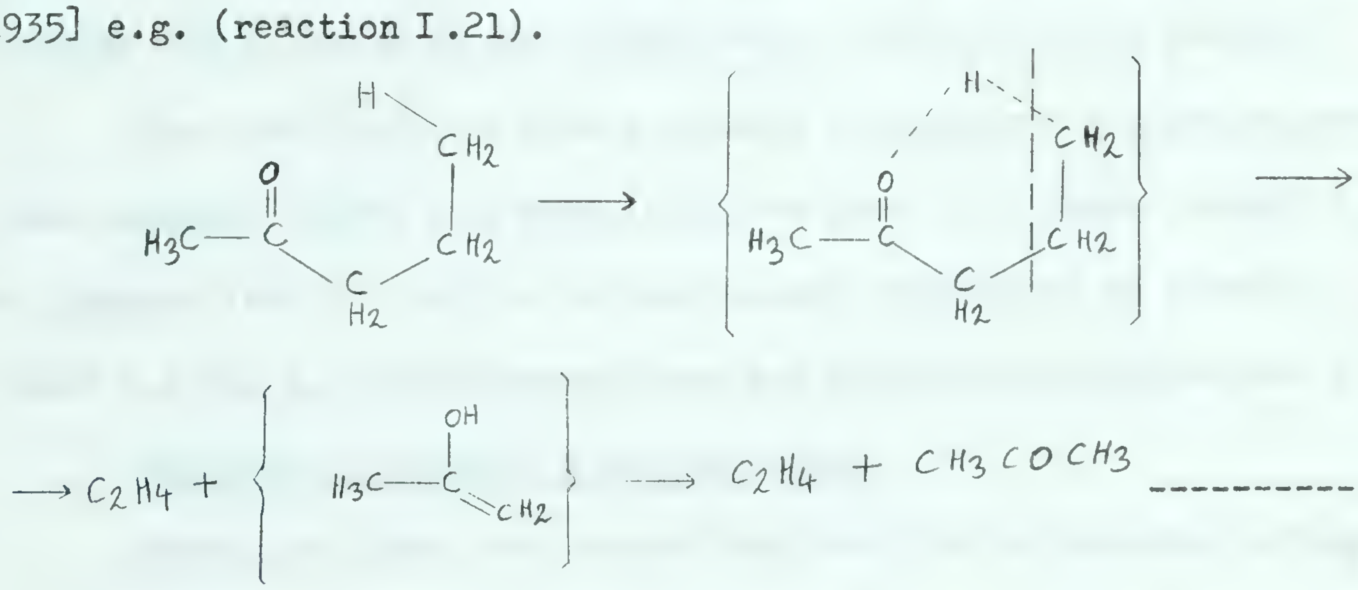
acts as a very good catalyst for many condensation reactions of acetone, [e.g. see Smith and Lindberg, 1931] and part of this difference in the results may be due to some impurities that may have been formed during the drying procedure.

The vapour phase radiolysis of acetone has also been investigated by Stief and Ausloos [Stief and Ausloos , 1961].

3. Miscellaneous.

The radiolysis of methyl ethyl ketone and of diethyl ketone has been studied [Ausloos and Paulson, 1958] and processes similar to those in the radiolysis of acetone seem to be operative.

Pitts and Osborne have compared the radiolysis of some saturated and unsaturated ketones [Pitts and Osborne, 1961]. They have suggested that some of the products from the saturated ketones arise from a γ-ray initiated rearrangement analogous to the photochemical intramolecular process for ketones [Norrish type II process; see Bamford and Norrish, 1935] e.g. (reaction I.21).



------------- (I,21)

Pitts and Osborne suggest that the same intermediate may be involved in both radiolysis and photolysis.

A significant observation in their investigation was the very low yields of gaseous products from cyclopropyl and the α,β unsaturated

ketones as compared to the saturated ketones. The values of G(gaseous products) were: dicyclopropyl ketone (0.36), methyl cyclopropyl ketone (0.62), methyl propenyl ketone (0.52), methyl n-propyl ketone (1.88), methyl n-butyl ketone (1.85) and methyl n-amyl ketone (2.24). They point out that the relative stabilities towards decomposition by radiolysis, exhibited by these ketones, are similar to the relative stabilities they exhibit towards photolysis. They suggest that the stability of the cyclopropyl ketones is due to the small ring substituents and the stability of methyl propenyl ketone is, in part, due to conjugation.

The gamma radiolyses of liquid n-butyrophenone, isobutyrophenone and benzoyl-cyclopropane have recently been investigated with regard to the formation of volatile products [Coyle, 1963]. No particular mechanism has been established though it has been tentatively concluded that the mechanisms for product formation during the radiolysis of these ketones are similar to those occurring during their photolysis at 2537Å (except for H_2 which is an insignificant product in the latter).

The radiolysis of dilute aqueous solutions of cyclohexanone has been examined [Serat and Mead, 1959] as part of a larger study to gain an insight into the action of high energy radiations on steroids. They found 1,2-and 1,3-cyclohexanediones and adipic acid amongst the products.

Ketones as hydrogen atom scavengers.

Strong and Burr have shown that addition of acetone is highly effective in reducing the yield of hydrogen from 2-propanol, whereas the yields of methane and CO are almost unaffected [Strong and Burr, 1959]. They conclude that the added acetone behaves as a hydrogen atom scavenger. Although the ionization potential of acetone (9.92 ev) is lower than that of 2-propanol (10.27 ev), they rule out the role of

acetone as an energy sink because of the lack of a disproportionate increase in the yield of CO from the acetone solutions and also because of the absence of biacetyl amongst the products, from the same.

Burr and Strong have also studied radiolysis of solutions of benzophenone in 2-propanol and conclude that the reduction in the yield of radiolytic hydrogen is caused by the H atom scavenging by benzophenone [Burr and Strong, 1959]. They have pointed out that benzophenone is more efficient than acetone in reducing the yield of hydrogen - a result also apparent from Hardwick's work [Hardwick, 1962] - but rule out energy transfer to benzophenone in favour of its increased H atom scavenging ability. They attribute the decrease in the yield of methane to the scavenging of methyl radicals by the aromatic rings of the benzophenone.

It has been suggested that in the radiolysis of binary solutions of cyclohexane and benzene, protection of cyclohexane by energy transfer to benzene is an important effect [Freeman, 1960; see also Manion and Burton, 1952 and Burton and Lipsky, 1957]. One further gets the impression that most aromatic compounds may act as energy sinks, in radiolytic systems [Swallow, 1960]. Thus, energy transfer might be an important process in the radiolysis of benzophenone solutions in 2-propanol.

Burr and Strong [Burr and Strong, 1959] have also discussed the formation of other products in the radiolytic system benzophenone in 2-propanol.

Hardwick studied the reactivity of hydrogen atoms with some ketones [Hardwick, 1962] and has found that, in the case of the aliphatic ketones studied, hydrogen addition occurred to a greater extent than did hydrogen abstraction. The value of the ratio of the rate of addition to that of abstraction was found to be about unity for acetone and about three for cyclohexanone.

D. <u>The Present Work.</u>

The radiolysis of cyclohexane has been widely investigated [e.g. see Dyne and Stone, 1961 and references therein] and the three major products are found to be hydrogen, cyclohexene and bicyclohexyl. The amounts of radiolytic products formed due to the opening of the ring of cyclohexane are very small; e.g. the G values for various products obtained recently in these laboratories [Ho and Freeman, 1963] are: hydrogen (5.39), cyclohexene (3.25), 1-hexene (0.43) and cyclohexyl-hexene - 1 (0.19). Thus, only about 11% of the cyclohexane that is decomposed by γ - rays seems to give products by ring opening. Similar conclusions can be drawn from the results of the radiolysis of methylcyclohexane [Freeman, 1962] where the extent of ring opening is about 16% of the C-H bond breakage.

These results suggest that the C_6 ring system in these two hydrocarbons is realatively stable towards ring opening as compared to the C-H bond breakage, despite the fact that C-C bond energies are in general lower than C-H bond energies [Cottrell, 1958].

A comparison of relevant bond energies [Cottrell, 1958] shows that the C-C and C-H bonds on a carbonyl carbon are weaker than comparable bonds in hydrocarbons (see Discussion).

In the case of cyclohexanone, if the oxygen atom did cause any weakness of the other bonds on the carbonyl carbon, then it would show up only in the C-C bonds since the carbonyl carbon has no hydrogens attached to it. Further, if radiolysis of this ketone gave evidence of increased ring opening it would indicate the dependence of primary radiolytic bond fission processes upon the relative bond dissociation energies in the molecule. It is hard to imagine any secondary reactions

that might cause such C-C bond rupture.

The radiolysis of cyclohexanone was therefore studied in the pure phase and in binary solutions with inhibitors. Benzene has been widely used as an inhibitor in radiolytic studies [Manion and Burton, 1952; see Swallow, 1960 and references therein] and it was suggested that it acts mainly as a protector by energy transfer in the radiolysis of hydrocarbons. However, Patrick and Burton studied the radiolysis of propionaldehyde in the presence of benzene [Patrick and Burton, 1954] and concluded that benzene does not protect propionaldehyde but sensitizes its radiolytic decomposition, and this was attributed to energy transfer from benzene to a low lying energy state of propionaldehyde. The photoionization potentials of benzene, propionaldehyde and cyclohexanone are 9.25, 9.98 and 9.14 ev respectively [Watanabe et al, 1962; compare, 9.21 (C_6H_6) and 10.06 (C_3H_6O) by electron impact; Field and Franklin, 1957] and they show absorption maxima in the near ultraviolet at about 260, 290 and 283 mμ respectively [Rao, 1961]. It was therefore considered interesting to see whether benzene would protect or sensitize the radiolytic decomposition of cyclohexanone.

It appeared that 2,3-dimethyl-1,3-butadiene might be a good radical scavenger [Brown and James, 1962] and this led to an investigation of its effect on the radiolysis of cyclohexanone.

Oxygen was primarily added to briefly compare its scavenging action with that of 2,3-dimethyl-1,3-butadiene. An added point of interest was provided by the observation [Srinivasan, 1959] that prior addition of oxygen increased the photolytic yield of 5-hexenal from cyclohexanone.

II. EXPERIMENTAL.

A. Apparatus.

1. High vacuum system.

A high vacuum system was assembled out of Pyrex glass as shown in Figures II.1 and II.2. It was supported by a metallic frame, sized 5'x 4½' x 1', that was mounted rigidly on a sturdy wooden table with a 5¼' x 3' flat top.

All glassware was cleaned with soap solution, followed by thorough rinsing with distilled water. Components that were to be used to store or irradiate liquids were cleaned with a hot mixture of sulphuric and nitric acids ($\sim$3:1), thoroughly rinsed with water and finally rinsed with double distilled water.

a. Main manifold.

A line diagram of the main manifold is shown in Figure II.1. A Welch duo-seal, two stage, vacuum pump with a free air capacity of 33.4 litres per minute, with a guaranteed vacuum of 1 micron or less, was used throughout these investigations. A Consolidated Electrodynamics Pirani vacuum gauge, type GP-110, was used. The narrow end of the Pirani gauge tube was mounted within a closely fitting Pyrex glass tubing with Picien Wax.

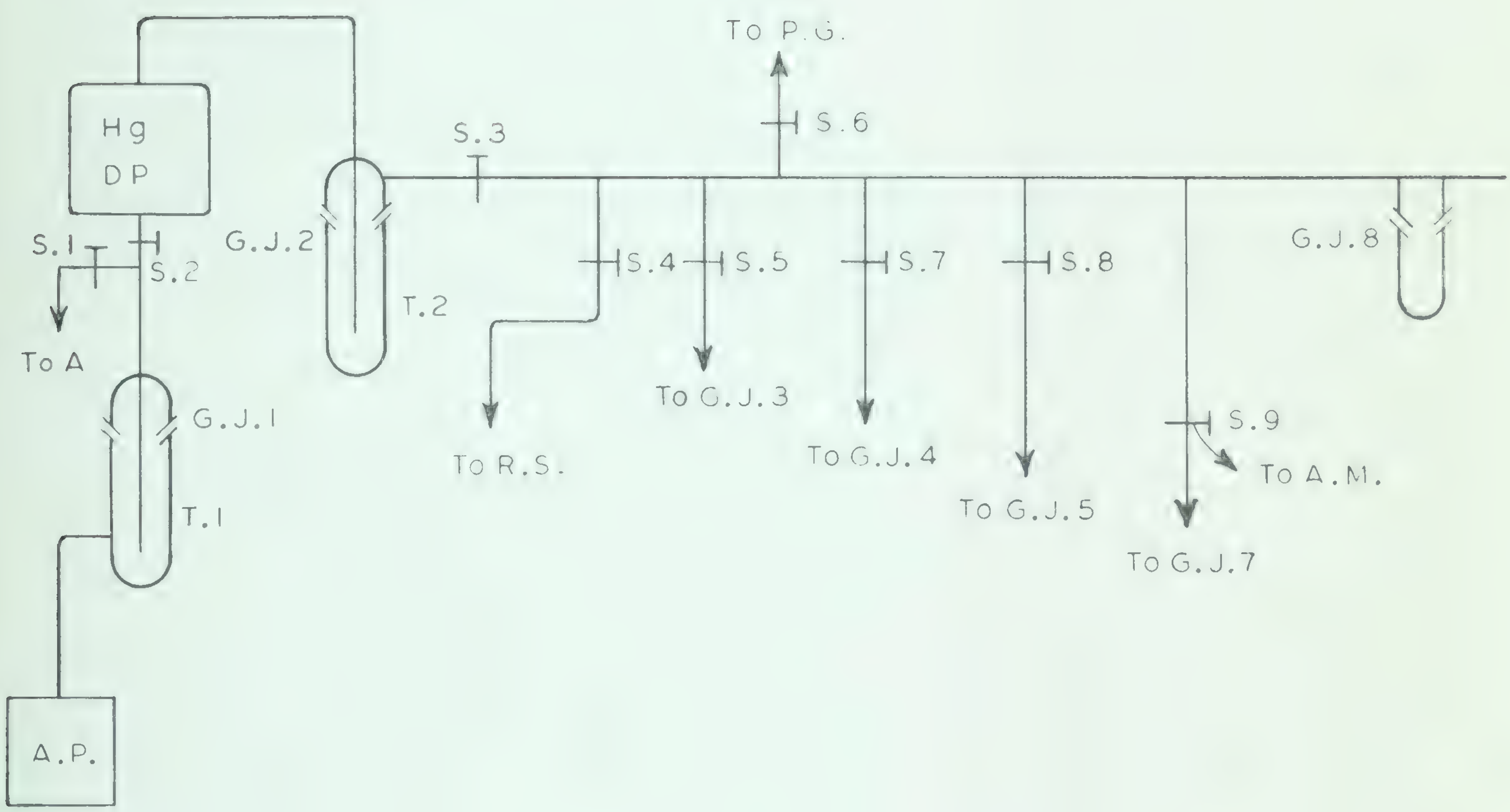
Initially Apiezon N grease was used on the B.45 ground glass joints GJ.1 and GJ.2 and on the 10 mm stop cocks S.2 and S.3. Later on, Silicone grease was used on S.2 and S.3 as it was found to last longer. Silicone grease was used on all other stop cocks and ground glass joints.

FIGURE II.1

Main Manifold

Figure not drawn to scale

A:	Air.
A.M:	Auxiliary manifold.
GJ.1-GJ.8:	Standard joints.
HgDP:	Mercury diffusion pump
P.G:	Pirani gauge
R.S:	Reservoir system
S.1-S.10:	Vacuum stop cocks
T.1 & T.2:	Traps
V.P:	Vacuum pump



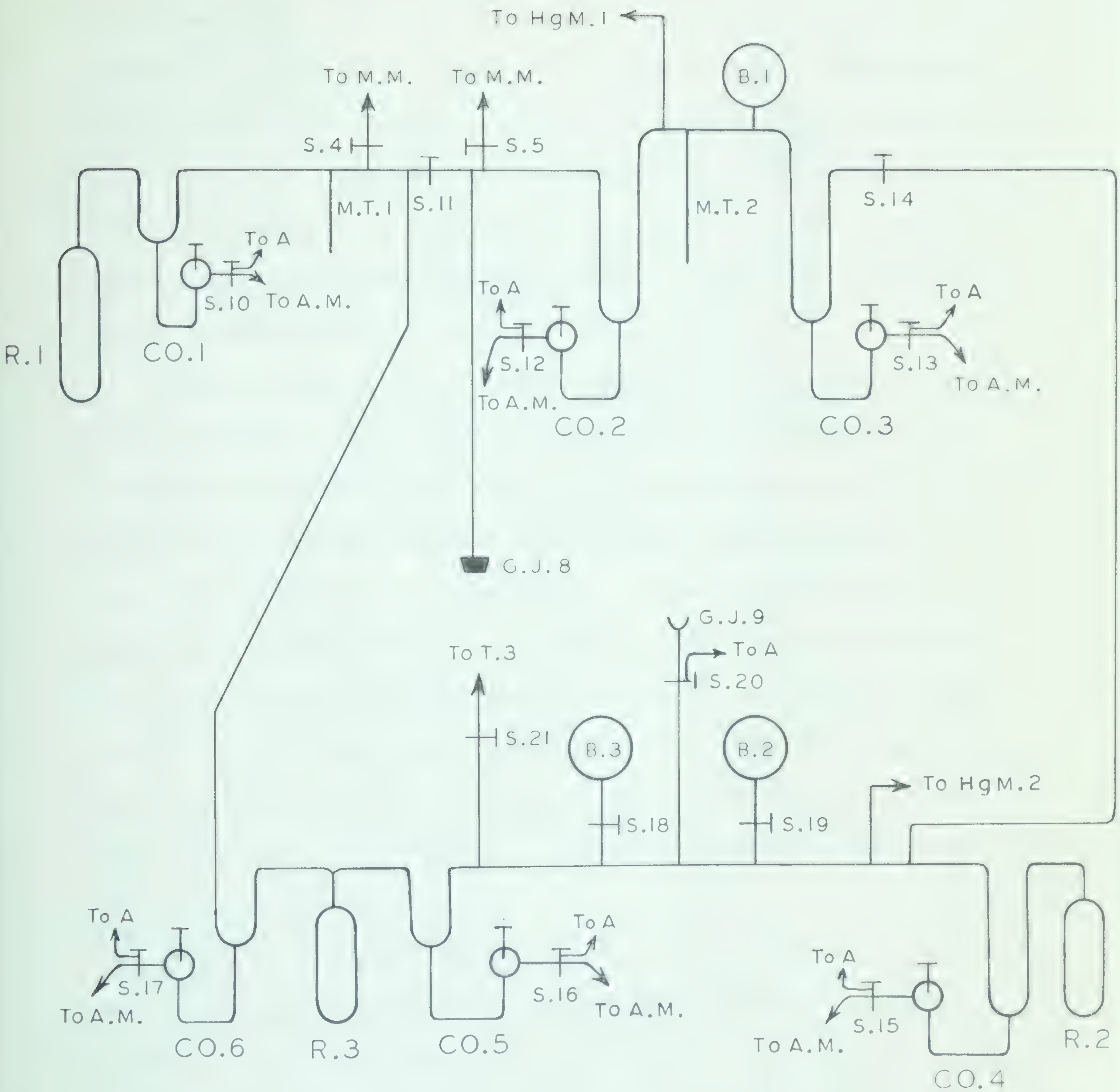
To P.G.
S.6
S.3
Hg
DP
S.1
S.2
To A
G.J.2
T.2
G.J.1
T.1
A.P.
S.4
S.5
S.7
S.8
G.J.8
To R.S.
To G.J.3
To G.J.4
To G.J.5
S.9
To A.M.
To G.J.7

FIGURE II.2

Reservoir System

Figure not drawn to scale

A:	Air.
A.M:	Auxiliary manifold.
B.1:	Calibrated bulb.
B.2 & B.3:	Storage bulbs.
CO.1 - CO.6:	Mercury cut offs.
GJ.8 & GJ.9:	Standard joints.
HgM.1 & HgM.2:	Mercury manometers.
M.M:	Main manifold.
MT.1 & MT.2:	Measuring tubes.
R.1 - R.3:	Reservoirs.
S.4 - S.21:	Vacuum stop cocks
T.3:	Trap



To HgM.1
To M.M.
To M.M.
B.1
S.4
S.5
M.T.1
S.11
M.T.2
S.14
To A
S.10
To A.M.
To A
To A
R.1
CO.1
S.12
S.13
To A.M.
To A.M.
CO.2
CO.3
G.J.8
G.J.9
To A
To T.3
S.20
S.21
B.3
B.2
To HgM.2
S.18
S.19
To A
To A
To A
To A
S.17
S.16
S.15
To A.M.
To A.M.
To A.M.
CO.6
R.3
CO.5
R.2
CO.4

b. Reservoir system.

Figure II.2 represents a line diagram of the reservoir system for liquids and gases. The system was also used for measuring the required amounts of the liquids or gases out of contact with air. Liquids were placed in or removed from the reservoirs by being vaporized through GJ.8. Gases were introduced into the storage bulbs B.2 and B.3 through GJ.9. All mercury cut offs, except CO.1, were Urry greaseless mercury float valve type with steel needle assembly. The cut off CO.1 was made from two commercial float valves.

Measuring tube MT.1 was used for measuring cyclohexanone. Ninety one, approximately, equally spaced marks were put on it by means of a diamond pencil and the total volume of the marked portion was 3.165 ml. Measuring tube MT.2 was used for measuring both liquid benzene and liquid 2,3 - dimethyl - 1,3 - butadiene. Fifteen, approximately, equally spaced marks were put on MT.2 and the total volume of the marked portion was 3.935 ml. Liquid level in between the marks was read with the help of a 1/32 inch scale mounted vertically along with the tube. The volume of bulb B.1 and the tubings, etc. between CO.2 and CO.3 was 333.0 millilitres; the pressure of a vapour in it could be read on the mercury manometer.

The vapour pressure of both benzene and 2,3 - dimethyl - 1,3 - butadiene is appreciable between $0^{\circ}C$ and room temperature. It was observed by a colleague [Eng, 1962] that serious errors could be caused in the amount of benzene taken, when measured in a system containing greased stop cocks. It was therefore decided to incorporate MT.2 and B.1 in the greaseless part of the system for measuring gases and liquids.

c. McLeod - Toepler gauge and traps.

Figure II.3a represents the distillation traps and the McLeod-Toepler gauge that were used for isolating and measuring the gaseous products. A float valve was incorporated in the design of the gauge between bulbs B.5 and B.6 to allow the gauge to be used as a Toepler pump. The volumes corresponding to various marks (Fig II.3a) on the McLeod-Toepler gauge are given in Table II.1.

TABLE II.1.

Calibrated volumes in the McLeod-Toepler gauge

Mark	Vol. in ml
M-1	0.179
M-2	0.538
M-3	6.965
M-4	64.45
M-5	581.0

Figures II.3b and II.3c represent the gas samplers used for collecting gaseous products from the McLeod-Toepler gauge for analysis. The gas sampler GS.1 was used for collecting the liquid nitrogen non-condensable products and GS.2 was used to collect the Dry Ice non-condensable products.

d. Auxiliary Manifold.

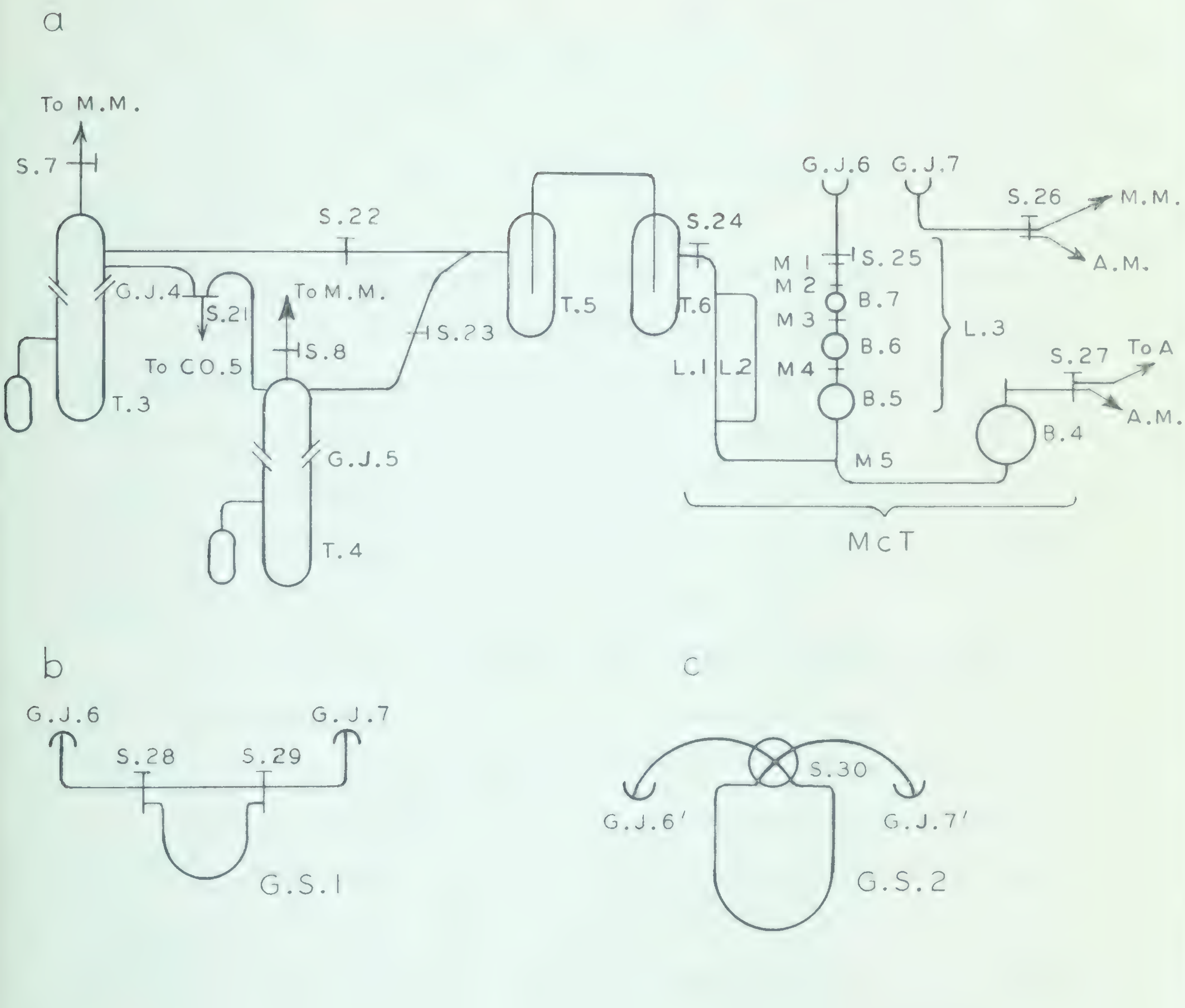
A Welch duo-seal, single stage, vacuum pump, with a free air capacity of 33.4 liters per minute and a guaranteed vacuum of 5 microns, was used to evacuate the auxiliary manifold. The main purpose of the auxiliary manifold was to operate the mercury cut offs and the McLeod-Toepler gauge. It also served to evacuate the gas samplers and to pump away unwanted gases from the McLeod-Toepler gauge. No cold traps were incorporated in

FIGURE II.3

McLeod-Toepler Gauge, Traps and Gas Samplers.

Figure not drawn to scale.

A:	Air.
A.M:	Auxiliary manifold.
B.4:	1 litre bulb.
B.5:	½ litre bulb.
B.6:	1/10 litre bulb.
B.7:	5 ml. bulb.
GJ.4 & GJ.5:	Standard joints (24/40).
GS.1 & GS.2:	Gas samplers.
L.1 - L.3:	Limbs of McLeod-Toepler gauge.
M.1 - M.5:	Marks on L.3.
McT:	McLeod-Toepler gauge.
M.M:	Main manifold
S.7 - S. 30:	Vacuum stop cocks.
T.3 & T.4:	Traps for breaking cells.
T.5 & T.6:	Traps for retaining liquids while separating gases. (i.e. -196^{o} fraction, etc.)



a
To M.M.
S.7
S.22
G.J.4
S.21
To CO.5
To M.M.
S.8
S.23
T.3
G.J.5
T.4
T.5
T.6
S.24
L.1
L.2
G.J.6
G.J.7
M 1
S.25
M 2
B.7
M 3
B.6
M4
B.5
L.3
S.26
M.M.
A.M.
S.27
To A
A.M.
B.4
M 5
McT
b
G.J.6
G.J.7
S.28
S.29
G.S.1
c
S.30
G.J.6′
G.J.7′
G.S.2

the auxiliary manifold.

2. Analytical instruments.

A Burrell Kromo-Tog model K2, with thermal conductivity cells was used for gas chromatographic analyses. Copper tubing or rubber pressure tubing was used for most of the connections for the carrier gas. Fine control needle valves (type LB1A, Edwards High Vacuum, Ltd.) were used to regulate the flow of carrier gas. A burette soap bubble meter was attached to the exit to measure the rate of flow of the carrier gas.

A tube, 21" long and 1" in diameter, containing calcium chloride was inserted in the path of the carrier gas before each of the Kromo-Tog purifying tubes, to help reduce the impurities in the carrier gas. Insulated heating wires, about 45 ft each (0.2 ohms/ft), were wound around the purifying tubes so that the tubes could be reconditioned by heating in the presence of slowly flowing carrier gas whenever necessary. Spent carrier gas was led off into a fume hood.

The voltage of the electric current supplied to the instrument was manually regulated to 116 ± 1 volts by means of a Powerstat. A voltmeter was put on the instrument to monitor the voltage being supplied.

Two and a half metre and 1 metre columns, supplied by Burrell Corporation, were used. Additional similar columns were made, as needed, from 6 millimetre inner diameter, heavy walled, Pyrex tubing. They were wound externally with Nichrome or Chromel heating wire (0.2 - 0.3 ohms/ft) to provide about 8 ohms resistance per metre of length of the columns.

A fraction collector, Burrell model 340-180, was used for collection of liquid products for identification purposes. The use of the trap (Burrell part no. 347-31) was found to be inconvenient. Therefore a metal fitting with a 7/15 taper at one end and a small bore, steel tubing at the

other, was made. This was used for collection of most of the liquid products.

Spectroscopic analyses in the infra-red region were done on a Perkin Elmer 421 Grating Spectrophotometer. Analyses in the ultraviolet and visible region were done on a Cary Recording Spectrophotometer, model 14M.

Mass spectral analyses were done on a Metropolitan Vickers Mass Spectrometer, Type MS 2.

3. Cobalt^{60} sources.

Source 1

The Co^{60} therapy unit at the Government of Alberta cancer clinic was used initially. Cells for irradiation could be placed in reproducible positions, in a Lucite block (Block A, Fig. II.4), in the beam collimator of the unit. The Lucite block was made by Freeman [Freeman,1959] and it had 14 holes (inner diameter, 16.0 mm) for cells to be irradiated. The block developed cracks and became fragile with use. The cells were exposed to the γ-rays from the source by remote control (electrically).

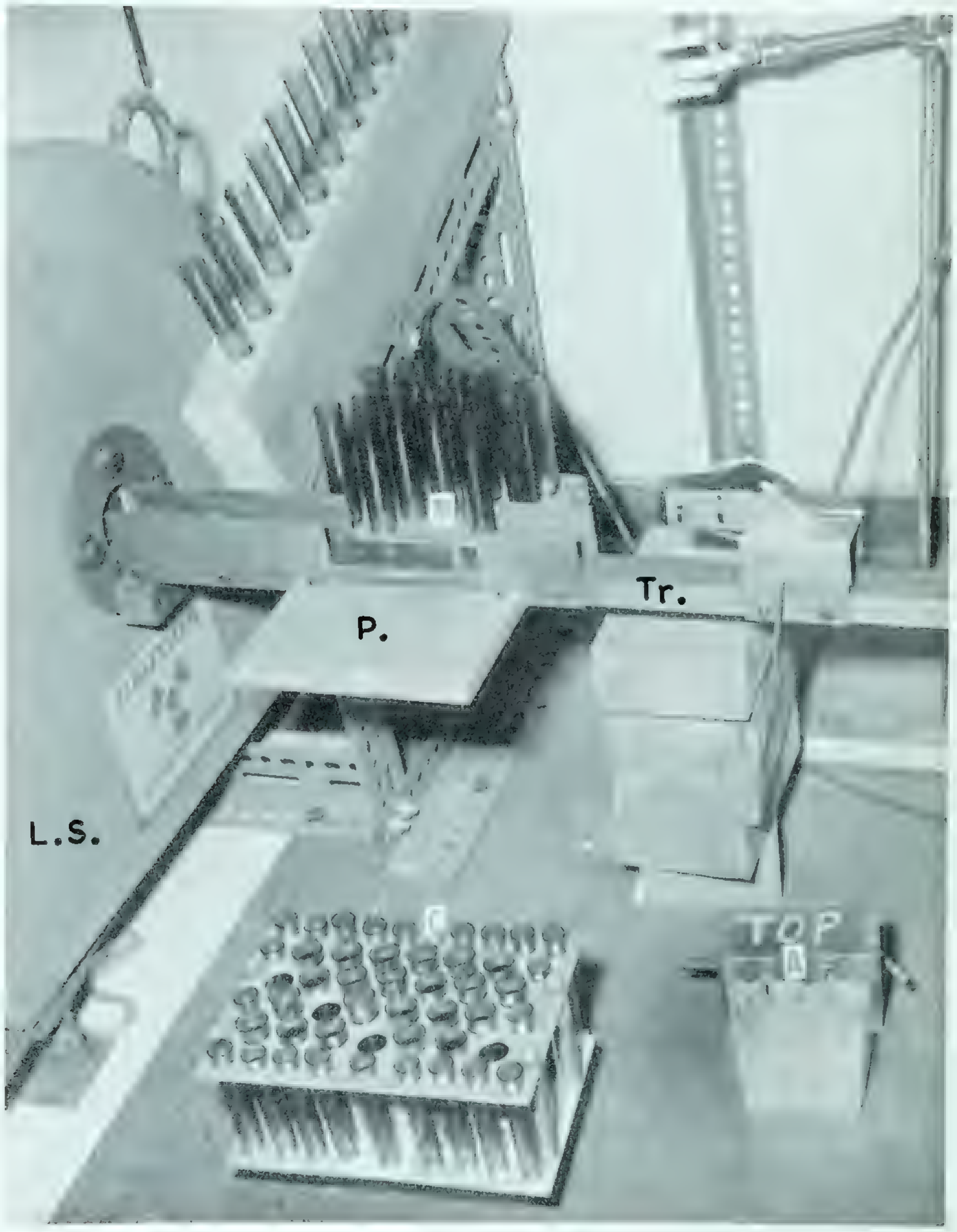
Source 2

Most of the irradiations were done in a specially built, heavy walled room in which a Co^{60} ($\sim$ 300 curies) source could be exposed. A sturdy steel track extended from the steel and lead shield of the source to the wall of the room and the source could be pushed out of the shield to a predetermined position on the track, from without the room, manually. Two sturdy plates ($\sim$6"x 4" each) were installed, one on either side of the track, on which the blocks (B and C) could be mounted in exactly reproducible positions. In Figure II.4, block B is mounted on one of these plates on the farther side of the track while block C can be mounted on the plate on the nearer side. The samples were placed in predetermined positions in either of the two blocks and the block was mounted on the

FIGURE II.4

Co^{60} Source 2 and the Irradiation Blocks

A:	Block A
B:	Block B
C:	Block C
L.S:	Lead and Steel shield of the source.
P:	Supporting plate for Block C.
Tr:	Steel track for the Source.


P.
Tr.
L.S.
TOP

appropriate plate followed by exposure to the source.

Block B (B, Fig. II.4) was made by a colleague [Wakeford, 1960] by placing Pyrex tubes of appropriate size in molten Wood's metal and allowing the metal to cool slowly to room temperature. Block C (C, Fig. II.4) [Myron et al, 1960] consisted of an aluminum frame in which Pyrex tubing of appropriate sizes was mounted through the holes in the upper plate on metallic pegs at the bottom.

B. Materials

A list of most of the materials used is given in Table II.2. Unless otherwise stated, they were used as supplied.

TABLE II. 2

Materials Used

No.	Name	By	Remarks (see after table)
1.	Acetylene	Matheson of Canada Ltd.	-
2.	Apiezon L on Firebrick	Burrell Corporation	-
3.	Apiezon Greases	Metropolitan-Vickers Electrical Co. Ltd.	-
4.	Arsenic Trioxide	National Bureau of Standards, U.S.A.	-
5.	Benzene	Phillips (Research Grade)	(iv)
6.	n - Butane	" " "	-
7.	1 - Butene	" " "	-
8.	Carbon disulpide	B.D.H. (For Infra-red Spectroscopy)	-
9.	Carbon monoxide	Matheson of Canada Ltd.	-
10.	Carbon tetrachloride	Eastman Kodak (Spectro Grade)	-

TABLE II. 2 (contd)

No.	Name	By	Remarks (see after table)
11.	Carborundum	Carborundum Co (60 SGM)	-
12.	Carbowax 1540	Carbide and Carbon Chemicals Co. Ltd.	(ii)
13.	Carbowax 20M	F.& M. Scientific Corporation	-
14.	Celite (Komat Ce)	Burrell Corporation	-
15.	Charcoal	" " (High Activity)	-
16.	Chloroform	Eastman Kodak (Spectro Grade)	-
17.	Chromotropic acid	K.& K. Laboratories Inc.	-
18.	Cyclohexanol	Fischer Scientific Company	(i)
19.	Cyclohexanone	Eastman Kodak (White label) Matheson Coleman & Bell Allied Chemical	(v)
20.	2-Cyclohexenone	Aldrich Chemical Co., Inc.	-
21.	Cyclopentane	Phillips (Research Grade)	-
22.	Cyclopropane	Matheson of Canada, Ltd.	-
23.	2,2'-Diketodicyclohexyl	Prepared as described.	(vi)
24.	2,3-Dimethyl-1,3--butadiene	Chemical Procurement Labs. Inc. K.& K. Laboratories Inc. Matheson Coleman & Bell	(vii)
25.	Di-tert-butyl peroxide	Matheson Coleman & Bell	-
26.	Ethane	Phillips (Research Grade)	-
27.	Ethylene	" " "	-
28.	Ferrous ammonium sulfate.	Allied Chemical	-
29.	Fluropak 80	The Fluorocarbon Co	-
30.	Formaldehyde solution	Fischer Scientific Company	-
31.	Helium	Air Reduction Canada, Ltd.	-

TABLE II.2 (contd)

No.	Name	By	Remarks (see after table)
32.	5-Hexen-2-one	Eastman Kodak(Yellow-Label)	(i)
33.	Hydrochloric acid	The Nichols Chemical Co. Ltd.	-
34.	Hydrogen	Canadian Liquid Air	-
35.	Iodine	B.D.H.(Analar)	-
36.	Mercury	Mallinckrodt (Triple distilled)	(viii)
37.	Methyl acetylene	Matheson of Canada, Ltd.	-
38.	Oxygen	Canadian Liquid Air	(ix)
39.	n-Pentane	Eastman Kodak (Yellow Label)	-
40.	n-Pentane	Phillips (Research Grade)	-
41.	1-Pentene	" " "	-
42.	2-Pentene	" " "	-
43.	Picien Wax	Edwards High Vacuum Ltd.	-
44.	Polyphenyl ether	F & M Scientific Corporation	-
45.	Poly-m-phenyl ether	Wilkens Instrument & Research Inc.	-
46.	Potassium iodide	Mallinckrodt	-
47.	Propane	Phillips (Research Grade)	-
48.	Silica gel	Burrell Corporation (Medium Activity)	-
49.	Silicone grease	Dow Corning	-
50.	Silicone rubber	Wilkens Instrument & Research Inc.	-
51.	Sodium chloride	Mallinckrodt	-
52.	Starch Soluble	"	-
53.	Sodium bicarbonate	"	-
54.	Sulfuric acid	The Nichols Chemical Co. Ltd.	-
55.	Ucon 75 H90000	Carbide & Carbon Chemicals Co. Ltd.	-
56.	Ucon LB-1800X	" " " "	(iii)
57.	Water.	(Double distilled)	[illegible]

Remarks from Table II.2

(i) Distilled before use.

(ii) Hereafter the term, 'Carbowax' refers to Carbowax 1540 only, unless otherwise stated.

(iii) Hereafter referred to as 'Ucon' only.

(iv) Benzene

Phillips Research Grade benzene was distilled before use. Gas chromatographic analysis, using Ucon, Carbowax, Silicone grease and Apiezon L columns, failed to reveal any impurities in it.

(v) Cyclohexanone

Qualitative analysis, [Smith and Jones, 1955], of cyclohenanone from various suppliers showed the absence of any major impurity in the ketone. Cyclohexanone from each supplier contained small amounts of water, a C_6 impurity, cyclohexanol, cyclohexenone and polymeric impurities. The impurities varied from bottle to bottle and from supplier to supplier. In general the ketone supplied by Allied Chemical was of the highest purity and that from Matheson Coleman and Bell was the least pure. The amount of impurities, particularly water and the C_6 impurity, seemed to increase when the ketone was left in contact with air.

The ketone was distilled using an 18" long fractionating column of 3/4" inner diameter and filled with glass helices. The middle 50% of the distillate was collected for redistillation. Single distillation reduced cyclohexanol and cyclohexenone content and removed all other impurities. Reduction in the amount of cyclohexanol was about 30% per distillation. Multiple distillations helped in reducing the amount of cyclohexanol and cyclohexenone, but led simultaneously to the formation of a small amount of an unidentified impurity (U.I.). This limited the purity obtainable by distillation. The purified ketone used in most of the investigations contained less than 0.02% impurities with each of U.I.,

cyclohexanol and cyclohexenone being less than 0.01%. The purity was checked by gas chromatographic analysis using Ucon, Carbowax, Silicone grease and Apiezon L columns.

Several modifications of the distillation procedure, e.g. distillation under reduced pressure, distillation under an atmosphere of nitrogen and distillation using a fractionating column containing Raschig rings, etc, did not make any significant difference in the purity of the distillate obtained.

Singly distilled ketone (impurities $<$0.04%) was used for large samples (10 ml) that were irradiated for the determination of the polymer formed.

Distilled ketone was kept in a desiccator until use.

(vi) 2,2'-Diketodicyclohexyl

This compound was prepared by the reaction of di-tert-butyl peroxide with cyclohexanone [Moore, 1951], (see section III.A.1c).

(vii) 2,3 - Dimethyl-1,3-butadiene

The diene was distilled under vacuum from a flask cooled in carbon tetrachloride slush (-25°C) into reservoir R.2 (Fig.II.2) kept cooled by liquid nitrogen. This procedure seemed to eliminate high boiling and polymeric impurities. It contained less than 0.5% impurities, as shown by gas chromatographic analysis on Ucon, Carbowax, Silicone grease and Apiezon L columns.

(viii) Mercury

It was found sufficient to pour mercury through a filter paper with a very small hole at the bottom, supported in a clean funnel, just before use. The filter paper was kept half filled with mercury, during this procedure. Floating impurities accumulated on the mercury in the filter paper and the last 25 ml of it was rejected. Initially some mercury was distilled under vacuum and was stored in clean bottles. But

a scum formed on its surface within about 48 hours and it had to be filtered, as outlined above, before use.

(ix) Oxygen.

Oxygen was passed through a Dry Ice cooled trap before being used.

(x) Double distilled water.

A two stage Pyrex distillation unit was used. The first distillation was done from a dilute solution of alkaline potassium permanganate, the distillate being redistilled. The double distilled water so obtained was carefully stored and was used for the Fricke dosimeter and for final rinsings of important glassware.

C. Procedure.

1. Operation of high vacuum system

Liquid nitrogen was normally used to cool trap T.1 (Fig. II.1) during evacuation of the system. A liquid nitrogen - Dry Ice mixture was used for overnight evacuation. Usually a pressure of one micron or less was obtained, as monitored by the Pirani gauge and checked occasionally by the McLeod-Toepler gauge. The evacuation time required to achieve a pressure of one micron or less could be reduced by also cooling trap T.2. with liquid nitrogen. However, as a matter of practice, this was resorted to only when necessary and was always followed up by overnight evacuation, with trap T.2 at room temperature, to remove any compounds that might have collected in T.2. Trap T.1 was cleaned periodically by rinsing with ether.

Ether was found to be more satisfactory than chloroform or carbon tetrachloride for cleaning stop cocks, etc, because it dissolved silicone grease better and because of its greater volatility.

2. Dosimetry.

The Fricke dosimeter was used to estimate the energy deposited in a sample by irradiation. A solution which was 0.4 molar in sulphuric acid, 1 millimolar in sodium chloride and 1 millimolar in ferrous ammonium sulphate was prepared using doubly distilled water. The electron density (moles of electrons per millilitre) of the solution was calculated and was found to be 0.565 at 25°C.

Source 1.

The dosimetry of this source was done by Freeman [Freeman, 1960]. The values for the energy absorbed by the Fricke dosimeter in various positions in the Lucite block are given in Table II.3.

Source 2.

B. Block

The irradiation cells used for dosimetry were made from 15.1+0.1 mm outer diameter Pyrex tubing in the shape of test tubes. One blank (unirradiated cell) was used with each set. The blank was allowed to stand in the laboratory while the others were irradiated in specified positions of the irradiation block. The irradiation time was 15 minutes for 2 ml and 4 ml cells and 20 minutes for 10 ml cells. The cells were kept covered with small clean beakers. Extreme care was used in handling the solution, both before and after the irradiations. All glassware used for dosimetry was cleaned with the hot mixture of sulphuric and nitric acids (see section II.A.1).

The absorption of the ferric ions formed during irradiation of the solution was measured [Hardwick, 1952]using a Cary Recording Spectrophotometer and a 5 mm quartz cell. The peak with its absorption maximum at about 304 $m\mu$ was scanned four times for each solution, and the average of the optical densities obtained was used. The spectrophotometer was used without a reference cell and readings with the blank were taken before

TABLE II.3.

Dosimetry

Source	Block	Position in Block	Volume of Solution in ml	Energy absorbed in 10^{18} e v /ml hr	Date of Estimation
1.	Lucite	1	1	1.04	June 20th,1959
1.	"	2	1	1.05	"
1.	"	3	1	1.03	"
1.	"	4	1	0.86	"
1.	"	5	1	0.88	"
1.	"	6	1	0.88	"
1.	"	7	1	0.86	"
1.	"	8	1	0.73	"
1.	"	9	1	0.74	"
1.	"	10	1	0.73	"
1.	"	11	1	0.60	"
1.	"	12	1	0.61	"
1.	"	13	1	0.61	"
1.	"	14	1	0.59	"
2	B	2	2	7.65	August 4th,1961
2	B	3	2	6.71	"
2	B	4	2	6.92	"
2	B	2	4	7.10	August 5th,1961
2	B	3	4	6.23	"
2	B	4	4	6.45	"
2	B	2	10	4.52	January 27th,1962
2	B	3	10	4.02	"
2	B	4	10	4.11	"
2	C	14	20	2.48	June 21st,1963
2	C	15	20	2.36	"

and after each set. The temperature of the cell chamber was recorded and each solution was allowed to attain that temperature before measuring its optical density.

The samples were placed 5cm away from the Co^{60} source during irradiation. The inverse square law variation of the intensity of the γ-rays in the sample was therefore appreciable because the sample thickness and height were greater than one centimetre. The irradiated solutions were shaken before making the measurements to ensure homogeneous sampling of the solutions.

The rate of energy absorption by the solution was calculated from the following expression.

Energy absorption in ev/ml hr =

$$= \frac{O.D.}{T} \times \frac{6.023 \times 10^{23} \times 2 \times 10^{2}}{2225\,[1 + 0.007 \times (t^{o} - 25)] \times 15.5 \times 10^{3}} \qquad \text{(II.1)}$$

where O.D. = Optical density of the solution,

T = Irradiation time in hours,

$G\ (Fe^{+++})$ = 15.5 [Swallow, 1960],

$\epsilon\ (Fe^{+++})$ = 2225 at 25°C [Hart et al, 1956],

and t^{o} = temperature in °C.

The values obtained for positions 2,3 and 4 in B block are given in Table II.3. Each of the values given is an average of three determinations. Corrections for the decay of the source were applied, when calculating the absorbed dose for samples at later dates, by using the expression II.2

$$N/N_{o} = e^{-\lambda t} \qquad \text{(II.2)}$$

where N/N_{o} = fraction of Co^{60} remaining.

$\lambda = 3.60 \times 10^{-4}\ day^{-1}$, (calculated from the half life of

5.27 years for Co^{60}, [Sulit, Leahy and Baietti, 1960]).

and t = time in days elapsed since determination of N_o.

C. Block.

Twenty millilitre samples for polymer estimation were irradiated in C block, for which results of dosimetry obtained by a colleague [Stover, 1962] were used. The values are given in Table II. 3.

Dose absorbed by cyclohexanone, etc.

The absorbed dose, in ev/ml, for cyclohexanone could be obtained using the expression (II. 3).

Dose absorbed by cyclohexanone = ...

$$= (\text{Dose absorbed by Fricke dosimeter in ev/ml hr}) \times \frac{e^- \text{ density of cyclohexanone}}{e^- \text{ density of Fricke dosimeter}} \times {}^{N}/_{N_o} \times \text{time of irradiation in hrs} \quad \text{------------------------} \quad (II.3)$$

The electron density of each solution of either benzene or 2,3-dimethyl-1, 3-butadiene in cyclohexanone had to be calculated separately.

3. Preparing samples for irradiation.

a. Storage and degassing of liquids.

(i) Cyclohexanone. About 100 ml of multiple-distilled cyclohexanone were taken in a flask with a $ 12/30 outer joint and put on GJ.8 (Fig. II.2). It was pumped upon for a few seconds through stop cock S.5, frozen in liquid nitrogen, and pumped upon again. It was degassed about fifteen times from liquid nitrogen. The degassing cycle consisted of three steps i.e. freezing, pumping upon the frozen ketone, then thawing followed by freezing and repetition of the cycle. The ketone was then distilled from a hot water bath into reservoir R.1 which was cooled with liquid nitrogen. It was degassed again fifteen times or so with the use of liquid nitrogen as the

freezing agent, followed by about twenty degassings using Dry Ice as the freezing agent. At the end of this it was observed that during thawing only about half a dozen small bubbles were evolved near the bottom of the liquid as the last bit of solid cyclohexanone melted, but these were reabsorbed by the liquid before reaching the surface. Further degassings, using either one of the two freezing agents, seemed to make no difference.

Cyclohexanone used for the first two sets of cells, that were irradiated with Source 1, was degassed from liquid nitrogen only. Blank cells in these sets gave a much larger value (0.179 ml at $\backsim$44 mm) of dissolved gases as compared to that from the blank cells from later sets (0.179 ml at $\backsim$ 4 mm) which were degassed from Dry Ice also, unless otherwise stated. The solutions of cyclohexanone and 2,3-dimethyl - 1,3-butadiene, used for making the 20 ml cells for estimation of polymer, were degassed using liquid nitrogen only, to avoid loss of the (pre-measured) diene during degassing.

(ii) Benzene

Freshly distilled benzene (100 ml) was taken in a flask with $ 12/30 outer joint and the latter was put on GJ.8 (Fig. II.2). It was degassed about 6 times using liquid nitrogen and was then distilled from the flask kept in luke warm water into reservoir R.3, which was kept cooled in Dry Ice. Degassing was continued after the distillation of benzene into R.3 with a slight variation of the degassing cycle, which now proceeded as — freeze with Dry Ice, pump upon it for a few seconds, cool in liquid nitrogen, thaw and repeat the cycle. A total of about twenty degassing cycles were carried out. No air bubbles were seen during thawing in the last five cycles.

(iii) 2,3-Dimethyl-1,3-butadiene

About 25 ml of the diene was degassed about 15 times, using liquid nitrogen as the freezing agent. It was distilled from a flask at -25°C

(carbon tetrachloride slush) into reservoir R.3, which was cooled in liquid nitrogen.

b. Filling cells for irradiation.

Pyrex tubing of 15.1 $\pm$ 0.1 mm outer diameter was used for making cells for irradiation. Use of 10 mm outer diameter heavy walled tubing for the neck of the cells made it convenient to seal the cells under vacuum. If a cell was to be used for analysis of gaseous products, it was made with a very thin bottom. It was found convenient to put each cell individually on GJ.8 (Fig. II.2) to be filled for irradiation.

Each cell was well evacuated, flushed with a very small quantity of cyclohexanone vapour and re-evacuated before being filled. The contents of the cell were then frozen with liquid nitrogen before the cell was sealed off, and were kept frozen while the sealed tip cooled slowly to room temperature thus avoiding possible pyrolysis of vapours which might come in contact with it.

Cyclohexanone was measured in the measuring tube (MT.1) at $0^{o}C$ before being distilled into an irradiation cell. Use of liquid nitrogen to cool the measuring tube, while cyclohexanone was being distilled into it from the reservoir, led to a slow accumulation of mercury in it. Dry Ice for cooling the measuring tube was found to be more satisfactory in this regard.

Cyclohexanone for one set of cells for irradiation at Source 1 and for all the cells for formaldehyde and polymer estimation was measured with calibrated pipettes at room temperature.

The density of cyclohexanone was calculated from the expression (II.4). [Brunel and Van Bibber, 1928].

$$d_t = [d_s + 10^{-3} \alpha (t - t_s)] \pm 10^{-4} \Delta \text{ --------------------- (II.4)}$$

where d_t = density at $t^\circ c$; t = given temperature;

d_s = density at t_s = 0.9625 gm/ml. $t_s = 0^\circ C$;

$\alpha = -0.855$; and $10^{-4}\Delta = 0.001$

Benzene was measured in the measuring tube (MT.2) as liquid and in the measuring bulb (B.1) as vapour, at room temperature, before being distilled into an irradiation cell. During distillation of benzene from the reservoir (R.2) into the measuring tube (MT.2), the latter was cooled with Ice-water. The density of benzene was calculated from the following expression [Brunel and Van Bibber, 1928].

$$d_t = [d_s + 10^{-3} \alpha (t - t_s) + 10^{-6} \beta (t - t_s)^2 + $$
$$+ 10^{-9} \gamma (t - t_s)^3] \pm 10^{-4} \Delta \text{ -------------------- (II.5)}$$

where d_t, d_s, t, and t_s have the same meaning as in expression (II.4)

and d_s = 0.90005 gm/ml; $\gamma = -2.213$

$\alpha = -1.0636$; and $10^{-4}\Delta = 0.0002$.

$\beta = -0.0376$;

The dimethylbutadiene was measured as liquid at $0^\circ C$ in the measuring tube (MT.2) and as vapour, at room temperature, in the measuring bulb (B.1). It was distilled from a carbon tetrachloride slush ($-25^\circ C$) cooled reservoir (R.3) to the chloroform slush ($-75^\circ C$) cooled measuring tube. Its density at $0^\circ C$ is 0.7446 gm/ml, [Patterson et al, 1961]. It was seen that measurement of the diene in B.1 followed by its transfer to a liquid nitrogen cooled irradiation cell was accompanied by the deposition of a small amount of mercury. It was considered necessary to avoid this deposition of mercury in the

samples to be irradiated for polymer estimation because the mercury might introduce an error in the weighing of the polymer. The diene was measured, therefore, with a calibrated 100 μl syringe before being added to the 20 ml cyclohexanone samples used for polymer estimation. It was assumed that the variation of the density of 2,3-dimethyl-1,3--butadiene could be represented by expression (II.6).

$$d_t = d_s + 10^{-3} \alpha (t-t_s) \text{ --------------------------------- (II.6).}$$

α was then calculated using Patterson's values [Patterson et al, 1961] for the two temperatures given. The density of the diene at room temperature was thus obtained.

For samples with added oxygen, a measured amount of cyclohexanone was distilled into the cell and was kept frozen with Dry Ice. Oxygen from B.2 was allowed into the cell, its pressure was recorded on the mercury manometer and the cell was sealed off.

4. Opening cells for analysis.

a. For ring fragmentation products.

The cell to be opened was placed carefully, with its thin end up, in trap T.3 (Fig. II.3). A cylindrical plunger of mild steel, about an inch long and half an inch in diameter, was placed very carefully on top of the cell. The trap was now put on GJ.4 and was evacuated till the pressure in the system fell to 1 micron or less. The stop cock (S.7) leading to the main manifold was now closed, and the trap was cooled with liquid nitrogen. During the next 10 minutes the pressure in this part of the system was checked a number of times with the McLeod-Toepler gauge. If there was no increase in pressure, then the traps (T.5 & T.6) between the cell and the McLeod-Toepler gauge were cooled with liquid nitrogen, the stop cock (S.24) following them was closed, liquid nitrogen

removed from around them and the liquid was distilled back into the cell bearing trap (T.3). Upon complete distillation of the liquid back into T.3, the whole cycle was repeated. At the end of this second cycle the volume, pressure and temperature of the gaseous products collected in the McLeod-Toepler gauge were recorded. The gases were then transferred to the previously evacuated gas sampler (GS.1), via stop cock S.25, by raising the mercury to just below the stop cock (S.25).

The products that were volatile at -150°C, -112°C or at - 70°C (hereafter called - 150°, - 112° and -70° fractions respectively), were collected in the McLeod-Toepler gauge by following a similar procedure and keeping isopentane slush, ethanol slush or Dry Ice, respectively, around the traps T.5 and T.6. In each of these cases, the products were transferred to the previously evacuated gas sampler (GS.2), but the sampler was cooled with liquid nitrogen.

Finally, the remaining liquid was distilled into the liquid nitrogen cooled side arm of the cell bearing trap (T.3), sealed off, and saved for analysis of the 'C_6' products. The liquid was not saved during the inhibition studies.

b. For C_6 and C_{12} products.

Cells for analysis of liquid products were filled and irradiated separately and were broken open at the neck just before use. They were corked and kept in a desiccator between injections of aliquots onto the gas chromatograph.

c. For products over C_{12}

The samples irradiated for the estimation of polymeric products, other than dimers, were 10 or 20 ml each. In general, each cell was broken open at its neck, put in a trap similar to T.3 and pumped upon

till all of cyclohexanone seemed to have evaporated. It was found that pumping upon the cell for twelve hours beyond this stage did not completely remove the last traces of cyclohexanone from the mixture of dimers and polymer. It was considered sufficient to pump upon each cell for four hours only, after all the cyclohexanone seemed to have evaporated, and this was adopted as a standard procedure. Then the cell was carefully taken out of the trap and weighed. The soluble contents of the cell were then removed by rinsing with three aliquots of about 1 ml each of Spectrograde chloroform. The resulting solution was poured into a 5 ml volumetric flask, and made up to 5 ml, for gas chromatographic analysis of its monomer and dimer content. The cell was placed in the trap again and pumped upon for some time to remove all the chloroform. The cell was then weighed, and the weight of the polymer was deduced from the loss of weight of the cell after due correction for the presence of monomer and dimers as estimated gas chromatographically. Some of these cells were analysed [Pascher, 1962] for insoluble polymer, by combustion.

Some cells were specially designed. The neck of such a cell culminated in a break-seal and a $\mathfrak{S}$ 24/40 outer joint, so that it could be pumped upon at GJ.4 (Fig. II.3) and the break-seal could be broken with the steel plunger, as in section 4a above, out of contact with air. The design of the cell kept the broken glass from falling into the liquid. These cells, were pumped upon in exactly the same manner as outlined in the previous paragraph, and upon requisite evacuation, were sealed off for C,H,O and molecular weight determination [Pascher, 1962].

5. Qualitative analysis.

a. Fragmentation products.

The identification of these products was based upon their gas chromatographic retention times, together with information from their infra-red and mass spectral analyses.

(i) Retention times.

Retention times of gaseous products of the -196° fraction were determined by repeated injections on a 1 metre high activity charcoal column, under specified conditions. This was followed by determination of the retention times of hydrogen and carbon monoxide on the same column under the same conditions. Helium was used as the carrier gas.

Retention times of components of the -70° fraction were determined by repeated injections on a 2½ metre medium activity silica gel column and on a 6 metre di-n-decyl phthalate column (on celite), under specified conditions. Retention times of over twenty C_1- C_5 hydrocarbons, and certain oxygen containing compounds, were also determined on these two columns for comparison. Hydrogen was used as the carrier gas.

(ii) Infra-red spectral analysis.

A 9 ml cell was irradiated to a dose of about 3×10^{20} ev /ml. The -112° fraction and the -70° fractions from this cell, were each collected separately in a previously evacuated Perkin Elmer cell for infra-red spectral analysis of gases, and the infra-red spectrum of each fraction was recorded.

(iii) Mass spectral analysis.

Figure II.5 represents a line diagram of the arrangement used for collecting individual gaseous products, as separated by the Silica gel column on the Kromo-Tog. Hydrogen was used as the carrier gas. The -70° fraction was initially contained in the gas sampler GS.2. The liquid nitrogen cooled trap T.7 was used to prevent the condensation of carbon

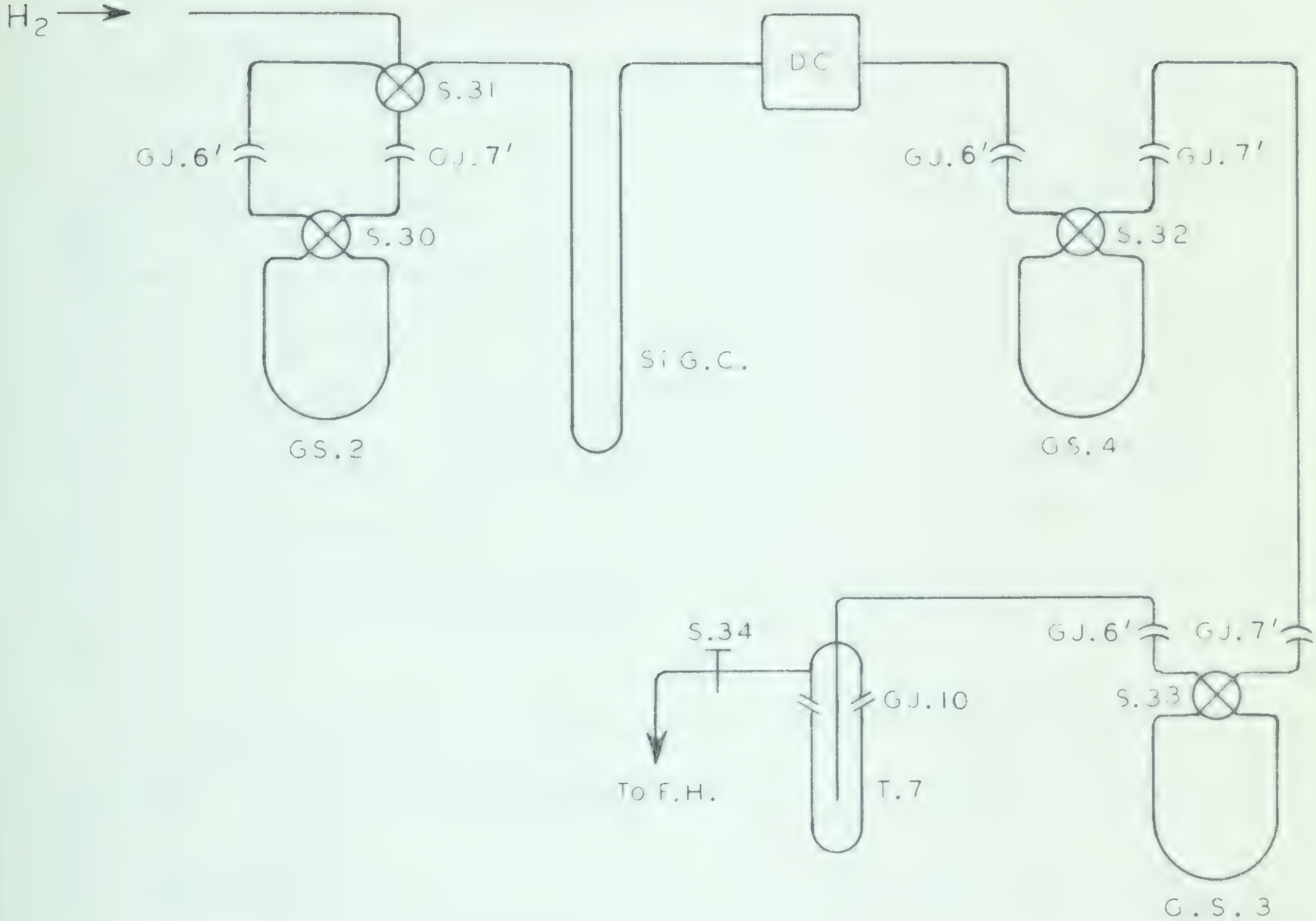
FIGURE II.5

Collection of Gaseous Products for

Mass Spectral Analysis

Figure not drawn to scale.

DC:	Detector cell.
FH:	Fume hood.
GJ.6' - GJ. 10:	Standard joints.
GS.2 - GS.4:	Gas samplers.
S.30 - S.34:	Vacuum stop cocks.
SiGC:	Silica gel column.
T.7:	Trap.



H_2
S.31
GJ.6′
GJ.7′
S.30
GS.2
Si G.C.
DC
GJ.6′
GJ.7′
S.32
GS.4
S.34
GJ.10
To F.H.
T.7
GJ.6′
GJ.7′
S.33
G.S.3

dioxide and water, from the atmosphere, in the gas samplers GS.3 and GS.4.

The gas samplers beyond the detector cell (GS.3 and GS.4) were flushed with the carrier gas and they were then cooled with liquid nitrogen. The carrier gas bypassed their U - section, thereafter, except when the products were being collected in either of them.

The Silica gel column was now conditioned and the upper part of GS.2 was flushed simultaneously with the carrier gas. When the column was ready for use, the - 70° fraction in the gas sampler GS.2 was injected upon the column and the products separated using temperature programming. Simultaneously with the injection, the stop cock S.33 of the gas sampler GS.3 was turned so as to collect the products from the outgoing carrier gas. An individual product for mass spectral analysis was collected in GS.4. Both GS.3 and GS.4 were kept in liquid nitrogen till the hydrogen had been evacuated from them. A re-run of the gases collected in GS.3 showed the extent to which a product had been collected in GS.4.

Four products were trapped off, separately, from the same mixture of gaseous products by repetitions of the procedure outlined above.

(iv) Formaldehyde.

The reaction of formaldehyde with Eegriwe's reagent [Eegriwe, 1937] was used for the detection of the aldehyde, according to the procedure described later in section C.6b(iii).

b. C_6 and C_{12} products.

The procedure for the identification of the liquid products was, in principle, similar to that used for the identification of the gaseous products. Irradiated cyclohexanone was injected on various columns under

specified conditions and the retention times of the products were measured. These were then compared with the retention times of known compounds injected on the same columns under the same conditions.

For infra red spectral analyses, various products were collected with the help of the modified fraction collector (referred to in section, II. A2 above) by passing the product bearing carrier gas through a small quantity of carbon tetrachloride (Spectro Grade). The resulting solutions were analysed with the Perkin Elmer 421 Grating Spectrophotometer. Some products were similarly collected for mass spectral analyses in carbon tetrachloride (Spectro Grade), but the solvent was removed before the analyses by evacuation at - 70°C.

For both infra red and mass spectral analyses it was found necessary to collect blanks from the column and compare the spectra of the blanks with those of the products.

The liquid contents of the 9 ml irradiated cell, mentioned in section 5a above, were distilled under vacuum into six fractions. However, the concentration of products in any of these fractions was not enough to be detected by infra red spectral analysis. The polymer remaining in the original cell, containing some dimer, was analysed for its infra-red spectrum and was also sent to Germany [Pascher, 1960] for quantitative analyses, (see section III.A.3b).

An effort was also made to qualitatively ascertain the presence of peroxides in the irradiated ketone. Both the ferrous thiocyanate method [Wagner et al,1947], and the iodometric method described by Siggia [Siggia, 1949] could not be used as cyclohexanone itself was found to interfere. Finally, the Arsenious oxide method [Siggia, 1949] was used as described later, (section II.6d).

6. Quantitative Analysis.

a. Gas chromatographic columns.

A column packing was prepared by dissolving the required amount of the partitioning agent in a solvent, usually ether, and adding the required quantity of the solid support to it in an evaporating dish. More solvent was added, if necessary, so that the solid support could be just submerged in the solution. The resulting slurry was mixed frequently as the solvent evaporated slowly, to insure homogeneous distribution of the partitioning agent on the solid support. Chloroform was found to be a better solvent for the carbowaxes. When preparing the Silicone rubber column the solid support, Silicone rubber, and petroleum ether (B.P. 60°- 80°) were added together and stirred till all of the petroleum ether had evaporated.

Bohemen and co-workers have found that tailing of polar compounds is reduced if the firebrick or celite used as solid support has been precoated with 0.1% polyethylene glycol (M400) [Bohemen et al, 1960]. In the present case precoating with Carbowax 1540, which is stable up to 150°C, was tried and found to give similar results. The precoated celite was used for di-n-decyl phthalate and Ucon columns.

A list of various columns tried for the gas chromatographic separation of the products of radiolysis of cyclohexanone is given in Table II.4.

All the columns mentioned in Table II.4 were tried under a variety of conditions e.g. various column voltage settings for temperature programming, various column voltage settings for analyses at constant temperature, and various flow rates of carrier gas. Hydrogen was used as the carrier gas, unless otherwise stated.

TABLE II.4

Columns Used

No.	Partitioning Agent	Concentration[a]	Length in metres	Solid support	Products for which tried
1.	Charcoal(High Activity)	-	1	-	H_2 and C_1
2.	Silical gel(Medium activity)	-	2½	-	C_2 to C_5
3.	Di-n-decyl phthalate	40	6	Celite	C_5 & C_6
4.	" "	6	2½	Fluoropak 80	C_6
5.	" "	15, 25	1	"	"
6.	Ucon LB-1800X	6	2½	"	"
7.	Carbowax 1540	6	2½	"	"
8.	Di-n-decyl phthalate	20,30,40,60,80,	1	Celite	"
9.	" "	20,40	2½	"	"
10.	Ucon 75 H90000	25	1	"	"
11.	Ucon LB-1800X	30,40	1	"	"
12.	" "	30	2½	"	C_6(& C_5)
13.	Carbowax 1540	30,40	1,2½	"	C_6
14.	Carbowax 20M	30	2½	"	C_6 & C_{12}
15.	Polyphenyl ether	30	2½	"	" "
16.	Poly-m-phenyl ether	30	2½	"	" "
17.	Silicone grease	25	1,2½	"	C_6, C_{12}(& C_5)
18.	Apiezon L	25	1	Firebrick	C_6 & C_{12}
19.	" "	20	1	Carborundum	" "
20.	Silicone rubber	60	2½	"	C_{12}

a. All concentrations of the partitioning agents are given as weight percent i.e. weight of the partitioning agent per 100 gm of solid support.

All concentrations of the partitioning agents are given as weight percent i.e. weight of the partitioning agent per 100 gm of solid support.

The 2½ metre Silica gel column separated the major constituents of -70° fraction very well. However, cyclopentane and n-pentane were not resolved. The 6 metre di-n-decyl phthalate column was found to separate cyclopentane from n-pentane, the latter giving a peak together with 1-pentene.

Columns using Fluoropak as the solid support had the advantage of greatly diminished tailing, as compared to tailing on celite. However, the packing seemed to get more and more tightly packed with use and the filling and unfilling of the columns was found to be very inconvenient. Also, the same partitioning agent on celite seemed to give better separations.

Carborundum was tried as a solid support for an Apiezon L column. Tailing of peaks on this was less than tailing of peaks on the Apiezon L column using firebrick as the solid support. However, the resolution of peaks on the two columns was not the same.

For Ucon and di-n-decyl phthalate columns, using celite as the solid support, 30%-40% concentration seemed to give the most satisfactory separations. The behaviour of Carbowax 1540 was very similar to that of Carbowax 20 M. The two polyphenyl ether columns did not seem to be useful for analyses of the irradiated ketone. The behaviour of the Silicone rubber column was similar to that of the Silicone grease column, but the latter was more efficient.

The following columns were chosen for the quantitative analysis of products. The detector cell was kept heated at 200°C throughout. Hydrogen was used as the carrier gas at a flow rate of 100 ml/minute, unless otherwise stated.

(i) Charcoal column.

This column was used for the analysis of the -196° fraction, at room temperature ($24 \pm 2^{\circ}C$), using helium as the carrier gas.

(ii) Silica gel column.

The silica gel column was used for the analyses of the -150°, -112° and -70° fractions. The column was used in the range 24°- $260^{\circ}C$ by temperature programming.

(iii) Di-n-decyl phthalate column.

The 6 metre di-n-decyl phthalate column was used, at constant temperature ($110^{\circ}C$) for the estimation of the cyclopentane content of the -70° fraction. It was also used at $150^{\circ}C$ for the estimation of 5-hexenal for a few samples.

(iv) Ucon column.

The 2½ metre, 30% Ucon column was used at $140^{\circ}C$ for the estimation of 5-hexenal and cyclohexanol. It was also used for the estimation of the sum of 1-pentene, 2-pentene and n-pentane, which were not resolved, in analysis of the radiolysis products of solutions of benzene in cyclohexanone.

(v) Carbowax column.

The 2½ metre, 30% Carbowax column was used at 135° for the estimation of cyclohexanol and cyclohexenone.

(vi) Silicone grease column.

The 2½ metre Silicone grease column was primarily used for the estimation of the dimeric products of the radiolysis of cyclohexanone. In some studies it was also used for the estimation of the C_5 products and also for the estimation of the disapppearance of 2,3-dimethyl-1,3--butadiene. It was used in the range 24°-$240^{\circ}C$ by temperature programming.

(vii) Apiezon L column.

The 1 metre Apiezon L column was primarily used for the estimation of total dimers, in the temperature range 24^{o} - 220^{o}C. The disappearance of 2,3-dimethyl-1,3-butadiene was also estimated using this column, during inhibition studies.

b. Calibrations.

(i) For ring fragmentation products.

All gases that were used for calibrations were measured in the McLeod-Toepler gauge before being transferred to the gas sampler. Data were obtained corresponding to the variation of the gas chromatographic peak area of each gas with the amount injected. Effort was made to inject such amounts of gases that their peak areas were of the same order of magnitude as the peak areas of the same products obtained during the analyses of the radiolysed samples.

Hydrogen and carbon monoxide were calibrated individually. For the calibration of the hydrocarbons, a number of mixtures of known composition were prepared.

On the basis of the data obtained, plots of the number of molecules of the gases versus their peak areas (versus peak height in the case of hydrogen) were made.

(ii) For C_6 and C_{12} products.

Standard solutions of known compounds were made in cyclohexanone. The cyclohexanone used for these solutions was from the same purified stock as that used for irradiation. All solutions were made by weight. Calibration factors were obtained from the variation of the peak area of a particular product with its concentration.

$$\text{Calibration Factor} = \frac{\text{Mole ratio of the compound}}{\text{Area ratio of the compound}} \quad \text{---- (II.7)}$$

where

$$\text{Mole Ratio of the compound} = \frac{\text{Moles of the compound}}{\text{Moles of cyclohexanone}}$$

and

$$\text{Area Ratio of the compound} = \frac{\text{Area of the compound peak}}{\text{Area of the cyclohexanone peak}}$$

Cyclohexanone was used as the internal standard. In most cases the calibration factor varied with the peak area, and plots of calibration factor versus peak area were made where necessary.

The concentrations of the known compounds were such that their peak areas were of the same order of magnitude as the peak areas of the same compounds in the radiolysed samples.

The calibration factor obtained for 5-hexen -2-one was used for the calculation of G values of 5-hexenal.

The Silicone grease column separated the C_{12} products to give seven different peaks. The C_{12} products gave only one peak on the Apiezon L column. Additional peaks of C_{12} products were obtained on analysis of the irradiated solutions of cyclohexanone in 2,3-dimethyl -1,3-butadiene. The calibration factors obtained for 2,2'-diketodicyclohexyl were used for all these C_{12} peaks.

<u>Special Cases</u>: <u>Calibrations for cyclohexanol and 5-hexenal during inhibition with benzene</u>.

The resolution of the cyclohexanol peak from the cyclohexanone peak, on both the Ucon and the Carbowax columns, was not very good and it depended upon the volume of the ketone injected. It was therefore necessary to determine a calibration curve for cyclohexanol for each different solution of cyclohexanone and benzene used. This was accomplished by injecting different volumes of the same standard

solutions of cyclohexanol on the two columns, such that the amount of cyclohexanone in the standard solution corresponded approximately to the amount of cyclohexanone in 100 μl irradiated benzene solution.

A similar problem was presented by the overlap of the tail of benzene peak and the 5-hexenal peak and was solved in essentially the same manner.

c. Analysis for formaldehyde.

Chromotropic acid [Eegriwe, 1937], in the presence of strong sulphuric acid, was used for the estimation of formaldehyde. The procedure used by Freeman [Freeman, 1961] was modified due to the high boiling point of cyclohexanone. The procedure finally used is given below.

Six 10 ml conical flasks were taken and 100 $\pm$1 mgm of chromotropic acid was weighed into each of them. Double distilled water (0.8ml) was added to each flask, followed by the addition of 0.20 ml of irradiated cyclohexanone to one of them, 0.20 ml of unirradiated cyclohexanone to another and 0.20 ml of standard solutions of formaldehyde to the other four flasks. The flasks were then suspended, with the bottoms submerged about 1 cm in an oil bath at 110 $\pm$ 2° C for fiften minutes. The temperature of the oil bath was raised during the next ten minutes to 150 $\pm$ 2°C and the flasks were heated at this temperature for fifteen minutes. They were then removed from the oil bath and allowed to cool to room temperature. Five millilitre of concentrated sulphuric acid were now added to each flask and they were heated in the oil bath again for thirty minutes at 130 $\pm$ 2°C. The flasks were then removed from the oil bath and allowed to cool. The acid solutions from the flasks were transferred into 25 ml glass stoppered flasks and 15.0 ml of double distilled water was added to each. The optical densities of the resulting solutions

were measured, within an hour, at 570 $m\mu$.

d. Peroxide estimation.

Procedure of Siggia [Siggia, 1949] was modified and used as follows.

In a 500 ml Erlenmeyer flask 10 ml of a standard (3.4×10^{-4} molar) arsenious oxide solution [Belcher and Nutten, 1960] was introduced containing 25 gm of sodium bicarbonate per litre. The sample (0.4 ml), in which peroxide was to be determined, was added to the flask followed by 10 ml of 98% ethanol. Boiling chips were added and the solution was heated to boil. It was kept gently boiling for 1½ hour, with occasional addition of double distilled water so as to keep its volume between 5 ml and 40 ml. At the end of 1½ hour of boiling the heat was stopped with about 5 ml solution left in the flask. It was allowed to cool to room temperature. When cold, it was made just acidic with 0.5 molar sulphuric acid followed by the addition of 0.5 gm of sodium bicarbonate. The excess arsenious oxide was then titrated with iodine solution [Belcher and Nutten, 1960] which was freshly standardized. Starch was used as the indicator. The endpoint was not sharp, the error in the endpoint being about $\pm$ 0.2 ml.

The calculations were done on the basis of the following stoichiometric equations:

$$2ROOR' + As_2O_3 + 2H20 = As_2O_5 + 2ROH + 2R'OH \text{---------------} \quad II.8)$$

$$2I_2 + As_2O_3 + 2H_2O = As_2O_5 + 4HI \text{------------------------} (II.9)$$

III. RESULTS.

A. Pure Cyclohexanone.

1. Qualitative analysis.

a. Fragmentation products

(i) Hydrogen and Carbon monoxide.

These were obtained together as the - 196° fraction and were characterized by their retention times on the Charcoal column.

(ii) Methane.

If methane were a product it should have been obtained with hydrogen and carbon monoxide in the -196° fraction. However methane could not be detected as a product by gas chromatographic analysis of this fraction on the Charcoal column in runs up to a dose of 3×10^{20} ev /ml. Therefore $G(CH_4) < 0.005$.

(iii) Retention times of hydrocarbons and products.

Retention times of twenty four hydrocarbons (C_1 - C_5) were obtained on the Silica gel column. The retention times of the constituents of the -70° fraction were compared with these and the products were identified as given below in order of appearance of their peaks using the Silica gel column.

1. Ethane
2. Ethylene
3. Propane
4. Acetylene
5. Cyclopropane
6. Propylene
7. n-Butane
8. Allene
9. 1-Butene
10. Cyclopentane
11. n-Pentane
12. Methyl acetylene
13. 1-Pentene
14. 2-Pentene

Allene was not available at the time these identifications were done. However a very small peak between n-butane and 1-butene could not be identified with any of the known hydrocarbons whose retention

times were determined. Recently Walker [Walker, 1963] has observed that the peak corresponding to allene appears in between the peaks corresponding to n-butane and 1-butene during the gas chromatographic analysis of these gases on a similar 2½ metre silica gel column. The previously unidentified small peak ($G < 0.001$) is therefore tentatively identified as allene.

Retention times of the hydrocarbons (C_1- C_5) were also obtained on the 6 metre di-n-decyl phthalate column, and these were compared with the retention times of the constituents of the -70° fraction, on the same column. In addition to the other products mentioned a small peak that corresponded to butadiene was observable at doses greater than $2x10^{20}$ ev /ml ($G < 0.001$).

Cyclopentane and n-pentane are not resolved by the Silica gel column. Work with the di-n-decyl phthalate column indicated that both of these might be present.

A minor product was visible just after 2-Pentene, on analysis of the -70° fraction from a large sample ($\sim$10 ml) using the Silica gel column. However, under the conditions used for quantitative analysis, this (unidentified) product is most likely to have been measured with 2-pentene.

These identifications were further supported by infra-red analyses of the gaseous product mixtures and by mass spectral analyses of some of the products.

(iv). <u>Infra-red analysis</u>.

The gaseous products from a 9 ml irradiated sample were collected in three fractions by distillations through traps at -196°C, -112°C and -70°C. Infra-red spectra of the -112° and -70° fractions were recorded and their interpretation [according to Bellamy, 1960] is summarized in Table III.1.

TABLE III.1.

Infra-Red Analyses of Gaseous Products.

Group Indicated	-112° fraction	-70° fraction	Indicated by Frequency (in cm^{-1}).
C-H (Aliphatic)	+[a]	+	various peaks in the 2800-3000 region
CH_3	+	+	2964
$C-CH_3$	+	+	1385, 1440[c] and 1455.[c]
$CH_2= CH$	+	+	3080(broad), 3010, 1410, 992, 982, and 908.
C=C	+	+	1655, and 1632.
C_2H_5	+	+	790[d]
$H_2C = CH_2$	+	+	3120[e] and 948[e].
CO	+	-[b]	2130, and 2160.
Impurity in the sampler	+	-	1730 - 1740.

a: + indicates presence in the fraction referred to.

b: - indicates absence in the fraction referred to.

c: These two peaks could not be observed in the -112° fraction as the spectrum was not recorded on the proper attenuation in that region.

d: According to Brügel [Brügel, 1962].

e: These peaks were found to be present in the spectra of ethylene, as obtained using the same instrument.

The system of traps (T.5 & T.6, Fig. II. 3) was not particularly suited to handle 9 ml of liquid. Therefore, the three fractions of gaseous products could not be separated from each other completely and a small amount of carbon monoxide seems to have been collected with the -112^{o} fraction giving rise to the doublet at 2130-2150 cm^{-1}.

The doublet at 1730-1740 cm^{-1} could not be identified with any of the products and appears to be due to an impurity in the gas sampler.

(v). Mass spectral analysis.

Identification of cyclopropane, propylene, n-pentane, cyclopentane and 1-pentene was confirmed by mass spectral analyses of these products as separated by the Silica gel column. The mass spectra so obtained were compared with those of the known hydrocarbons and are summarized in Tables III.2 and III.3. The values of the abundance of various ions are given as the percentage fraction of the largest peak, and where the values for a particular ion are less than 3% for all the compounds listed in the Table, they have been omitted.

b. C_6 products.

(i). 5-Hexenal.

The gas chromatogrphic peaks corresponding to 5-hexen-2-one, n-hexanal and 2-hexenal appeared close together in a small region on the chromatograms, well before the cyclohexanone peak, upon separation by the Ucon column. A product of the radiolysis of cyclohexanone gave a gas chromatographic peak in the same region upon separation by the same column. However, its retention time did not agree with that of any of these three compounds. Similar results were obtained upon separations by the Carbowax column and by the di-n-decyl phthalate column.

TABLE III.2

Mass Spectral Analyses of Cyclopropane and Propylene.

m/e	1	2	3	4
14	2.9	7.4	1.8	3.6
15	2.6	5.8	2.8	5.4
26	15.3	14.4	10.8	10.5
27	28.0	37.2	31.2	38.3
28	6.7	2.9	20.4	1.3
32	9.0	0.0	7.5	0.0
37	8.8	10.5	11.9	13.6
38	12.3	15.1	17.7	19.3
39	60.7	69.5	69.0	71.1
40	29.9	31.2	31.6	28.9
41	89.2	89.1	100.0	100.0
42	100.0	100.0	72.1	67.7
43	5.3	3.4	6.3	2.2
44	10.3	0.1	6.8	0.0

m/e: Mass of the ion/charge of the ion.

1: Product considered to be cyclopropane, separated gas chromatographically. The large value for m/e = 44 is probably due to CO_2, collected during the trapping procedure.

2: Cyclopropane, [A.P.I., 1956; Serial no. 115].

3: Product considered to be propylene, separated gas chromatographically. The large values for m/e = 28, 32 and 44 indicate that air might have leaked into the gas sampler.

4: Propylene, [A.P.I., 1956; Serial no. 24].

TABLE III.3

Mass Spectral Analyses of Cyclopentane,

n-Pentane and 1-Pentene.

m/e	1	2	3	4	5	6	7	8
15	1.7	1.9	1.1	5.6	1.1	6.0	6.0	3.2
26	2.1	3.0	1.9	5.5	1.9	4.7	4.6	4.4
27	25.1	23.3	9.0	32.3	23.9	28.7	27.6	14.8
28	4.6	7.3	2.5	4.9	5.1	4.8	4.7	1.9
29	19.4	15.6	3.7	27.0	22.6	29.3	28.5	0.9
38	1.3	1.5	2.2	4.5	4.0	4.4	4.2	8.5
39	12.5	20.5	16.5	34.6	32.4	33.1	31.7	36.4
40	2.5	6.6	6.3	8.6	8.5	5.8	5.6	15.9
41	39.8	48.2	26.5	45.0	44.5	29.0	30.3	19.0
42	57.2	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	45.9	43.7	8.4
43	<u>100.0</u>	65.5	4.1	4.1	4.9	2.1	2.1	0.3
44	3.4	3.2	0.0	0.1	0.4	0.0	0.0	0.0
52	0.2	0.4	0.1	0.7	3.2	1.0	1.0	1.5
53	1.0	2.2	1.8	4.7	5.3	7.7	7.5	23.4
55	3.4	22.8	31.4	57.9	61.6	<u>100.0</u>	<u>100.0</u>	0.0
56	2.3	4.8	1.4	2.6	2.8	4.3	4.4	0.0
57	13.6	8.8	0.0	0.1	0.2	0.1	0.1	0.0
66	0.0	0.2	0.3	0.2	0.4	0.6	0.3	9.5
67	0.0	1.1	1.8	1.1	2.4	1.8	1.8	<u>100.0</u>
68	0.0	0.3	0.5	0.2	0.2	0.3	0.3	41.6
70	0.4	19.8	31.2	31.7	36.4	33.6	33.4	0.1
72	8.6	5.9	0.0	0.0	0.1	0.0	0.0	0.0

TABLE III.3 contd

1: n-Pentane, Research Grade

2: Product considered to be a mixture of n-pentane and cyclopentane, separated gas chromatographically.

3: Cyclopentane, Research Grade

4: 1-Pentene, [A.P.I., 1956, Serial No. 29].

5: Product considered to be 1-pentene, separated gas chromatographically.

6: 2-Pentene (cis), [A.P.I., 1956, Serial No. 30]

7: 2-Pentene (trans), [A.P.I., 1956, Serial No. 31]

8: Cyclopentene, [A.P.I., 1956, Serial No. 208]

Retention times of various organic compounds were obtained on the three columns. If the product in question were a C_6 carbonyl compound containing a C_5 ring system it would most probably have appeared closer to the cyclohexanone peak, since cyclopentanone peak appears (Ucon and di-n-decyl phthalate columns) after the region of the peaks of 5-hexen -2-one, etc. On the other hand, if it were a C_6 ether it should have appeared before the region of 5-hexen-2-one, etc, on the Carbowax column.

It was therefore thought that the product was 5-hexenal. An authentic sample of 5-hexenal could not be obtained commercially for comparison.

The product considered to be 5-hexenal was collected after gas chromatographic separation on the Ucon column, for infra-red spectral analysis. The infra-red spectrum indicated the presence of $CH_2 = CH$ (bands at 3070-3080 cm^{-1}, and 905 cm^{-1}), C=C (band at 1638 cm^{-1}), aldehydic C-H (bands at 2710 cm^{-1} and 2810 cm^{-1}), and C=O (band at 1714 cm^{-1}). If this product were an α,β unsaturated aldehyde the CO vibrations should have been in the 1680-1705cm^{-1} region, and if this product had contained a ketonic group in a four or five membered ring the CO vibrations should have been in the 1740-1775 cm^{-1} region. So that the infra-red spectrum obtained is consistent with the identification of the product as 5-hexenal.

The product considered to be 5-hexenal was also separated gas chromatographically on the di-n-decyl phthalate column and on the Carbowax column for infra-red spectral analyses with similar results.

The product considered to be 5-hexenal was separated, using the Ucon column, for mass spectral analysis. A 'blank' from the column was collected for 240 seconds while the 5-hexenal peak was collected for

112 seconds. The 'blank' was assumed to be uniform during the two collections. The mass spectral data are recorded in Table III.4 along with the mass spectral data of 5-hexenal obtained by Srinivasan [Srinivasan, 1961]. The values of the abundance of various ions are given as the percentage fraction of one of the larger peaks and where the values for a particular ion are less than 3% for all the compounds listed in the Table, they have been omitted. The values in column 1 refer to the blank and correspond to the peak heights represented as a percentage of the largest peak (m/e = 55). The value of the m/e = 55 peak in the trapped product (column 2) was also set at 100.0 and the values of the other peaks were calculated relative to it.

It was found that by subtracting 46.3% of the values given in column 1 from those in column 2, the values of the product peaks of m/e = 54 and 55 matched those given by Srinivasan [Srinivasan, 1961]. The rest of the mass spectrum of the product was obtained by subtracting 46.3% of the values of the blank peaks from the corresponding values of the product peaks. The mass spectrum of the product (column 4) agrees quite well with that of 5-hexenal (column 5), [Srinivasan, 1961].

Values of ions from water (m/e = 17 and 18), air (m/e=28,32 and 44) and carbon tetrachloride (m/e = 35-37, 47, 49, 82-86 and 117-123) have been omitted. Values for cyclohexanone for the ions listed are included (Table III.4) for comparison. It may be observed that the mass spectrum of the blank is quite similar to the mass spectrum of cyclohexanone.

On the basis of the supporting evidence from the infra-red and the mass spectral data, the product in question is considered to be 5-hexenal.

TABLE III.4

Mass Spectral Data concerning 5-Hexenal Identification

m/e	1	2	3	4	5	6
14	1.7	6.2	0.8	5.4	3.2	0.9
15	0.7	3.7	0.3	3.4	10.6	2.2
16	4.1	5.3	1.9	3.4	0.0	0.0
26	3.1	7.4	1.4	6.0	8.4	3.7
27	15.6	53.8	7.2	46.6	52.7	19.1
29	6.7	55.3	3.2	52.1	59.5	6.7
38	7.6	9.8	3.5	6.3	5.3	2.4
39	21.8	89.4	10.3	79.1	62.3	19.8
40	6.6	15.6	3.1	12.5	8.5	6.1
41	31.8	112.2	14.8	97.4	94.0	29.4
42	70.6	81.9	32.8	49.0	41.2	73.4
43	11.7	69.3	5.4	63.9	27.1	11.2
45	0.1	13.5	0.0	13.4	0.0	0.0
50	1.5	4.1	0.7	3.4	2.4	1.4
51	1.8	6.1	0.9	5.2	3.3	1.8
53	3.1	14.3	1.4	12.9	10.8	2.8
54	6.9	103.2	3.2	<u>100.0</u>	<u>100.0</u>	7.5
55	<u>100.0</u>	100.0	46.3	53.7	53.7	<u>100.0</u>
56	11.6	23.0	5.4	17.6	13.1	11.8
57	2.0	20.5	1.0	19.5	15.4	1.5
58	0.2	5.7	0.1	5.6	1.6	0.1
67	1.2	7.4	0.6	6.8	4.3	1.3
69	25.7	32.8	11.9	20.9	19.9	37.5
70	22.8	22.6	10.6	12.0	12.3	21.2

Table III.4 contd.

m/e	1	2	3	4	5	6
71	1.9	4.1	0.9	3.2	2.7	1.8
73	0.0	6.1	0.0	6.1	5.8	0.0
79	0.8	6.1	0.4	5.8	3.7	0.7
80	4.3	43.4	2.0	41.4	33.2	4.1
81	0.5	3.7	0.2	3.5	2.2	0.4
91	0.1	8.6	0.1	8.5	0.0	0.0
92	0.0	6.1	0.0	6.1	0.0	0.0
97	2.2	4.9	1.0	3.9	1.6	4.0
98	18.6	19.7	8.6	11.1	3.3	38.6

1: Blank

2: Product considered to be 5-hexenal.

3: Values for blank multiplied by 0.463.

4: Column 2 minus Column 3; i.e. corrected values for the product considered to be 5-hexenal.

5: Values for 5-hexenal, [Srinivasan, 1961].

6: Mass spectrum of cyclohexanone.

(ii) Unidentified impurity (U.I.)

The unidentified impurity in cyclohexanone, which decreased with increasing dose during radiolysis, upon separation by the Ucon column gave a gas chromatographic peak that was a doublet. Gas chromatographic separation by the di-n-decyl phthalate column confirmed that it was a mixture of two substances. On the basis of the retention times of various compounds on the two columns, it seemed likely that the impurity might belong to any of the following three types of compounds: C_6 carbonyl compound with a C_5 ring system, C_6 open chain alcohol or C_7 open chain carbonyl compound. Its infra-red spectrum was examined, after separation by the Ucon column, which indicated the presence of C=C (1638cm^{-1}) and a CO in a C_5 ring (1740cm^{-1}). After separation on the Ucon column and collection during 142 seconds ('blank', 240 seconds), its mass spectrum was obtained. The mass spectral data are recorded in Table III.5.

A comparison of the mass spectrum of the impurity with those of the blank, 5-hexenal and cyclohexanone shows that its fragmentation pattern is different from the fragmentation patterns of both 5-hexenal and cyclohexanone. A reasonable basis for the deduction of blank values from the values of the impurity could not be found in this case.

In the treatment hereafter it will merely be regarded as an unsaturated impurity and referred to as 'U.I'.

(iii) Cyclohexanol.

Cyclohexanol was characterized as a product of the radiolysis of cyclohexanone by its retention times on the Ucon, the Carbowax, the di-n-decyl phthalate and the Silicone grease columns. The addition of a very small quantity of cyclohexanol to the radiolysed cyclohexanone

TABLE III.5

Mass Spectral Data of U.I. and Other Compounds

m/e	1	2	3	4
12	4.8	5.2	0.0	0.0
14	1.7	9.1	5.4	0.9
15	0.7	2.5	3.4	2.2
16	4.1	6.0	3.4	0.0
26	3.1	4.3	6.0	3.7
27	15.6	31.0	46.6	19.1
29	6.7	31.5	52.1	6.7
36	15.8	19.8	0.4	0.0
38	7.6	7.8	6.3	2.4
39	21.8	36.2	79.1	19.8
40	6.6	11.6	12.5	6.1
41	31.8	69.4	97.4	29.4
42	70.6	78.0	49.0	73.4
43	11.7	60.4	63.9	11.2
45	0.1	6.5	13.4	0.0
51	1.8	3.4	5.2	1.8
53	3.1	8.2	12.9	2.8
54	6.9	16.8	100.0	7.5
55	100.0	100.0	53.7	100.0
56	11.6	23.7	17.6	11.8
57	2.0	35.0	19.5	1.5
58	0.2	5.6	5.6	0.1
67	1.2	10.3	6.8	1.3

TABLE III.5 (contd)

m/e	1	2	3	4
68	1.0	5.2	0.0	0.0
69	25.7	38.8	20.9	37.5
70	22.8	27.6	12.0	21.2
71	1.9	15.5	3.2	1.8
72	1.4	3.5	0.0	0.0
73	0.0	0.0	6.1	0.0
79	0.8	4.7	5.8	0.7
80	4.3	9.1	41.4	4.1
81	0.5	8.6	3.5	0.4
91	0.1	4.7	8.5	0.0
95	0.5	7.8	1.8	0.0
96	0.1	3.9	1.6	0.2
97	2.2	11.4	3.9	4.0
98	18.6	33.2	11.1	38.6
99	2.4	3.5	0.1	2.5
105	0.1	6.0	0.0	0.0
109	0.0	2.6	0.0	0.0
110	0.1	1.3	0.0	0.0
111	0.0	0.9	0.0	0.0
113	0.0	0.2	0.0	0.0

1: 'Blank'.

2: Product considered to be 5-hexenal.

3: 5-hexenal.

4: Cyclohexanone.

caused the peak considered to be cyclohexanol to grow in size. The product considered to be cyclohexanol was separated gas chromatographically using the Ucon, the Carbowax and the di-n-decyl phthalate columns for infra-red spectral analyses. Cyclohexanol is not separated completely from large quantities of cyclohexanone by any of these columns. Thus the presence of larger proportions of impurities in the product collected did not allow meaningful conclusions to be drawn from the infra-red spectra obtained.

(iv) Cyclohexenone.

Cyclohexenone was characterized as a product by its retention times on the Ucon and the Carbowax columns. The product considered to be cyclohexenone was separated using the Carbowax column for infra-red spectral analysis. The infra-red spectra showed the presence of C=C-C=O (peak at 1686 cm^{-1}) and CH=CH(peaks at 3015 cm^{-1}, 1305cm^{-1}, and 665 cm^{-1}[Cross, 1960])thus indicating the presence of 2-cyclohexenone. However, the possibility of the presence of 3-cyclohexenone cannot be ruled out on the basis of this work.

c. C_{12} products.

(i) Preparation and analysis of 2,2'-diketodicyclohexyl.

This compound was prepared by the reaction of di-tert-butyl peroxide with cyclohexanone [Moore, 1951]. Initially it was separated from the reaction mixture gas chromatographically. In later work it was also obtained by vacuum distillation of the reaction mixture.

Gas Chromatographic Separation.

The reaction mixture upon separation on the 1 metre Apiezon L column (using carborundum as the solid support) gave a big peak preceded by one small peak and followed by two others, in a region well beyond the cyclohexanone peak. The infra-red spectra of the products corresponding to these four peaks were very similar. However, the products

corresponding to the small peak after the big peak seemed to be unsaturated (bands at $3070cm^{-1}$ and $1678cm^{-1}$). The product corresponding to the big peak was taken to be 2,2'-diketodicyclohexyl and the smaller peaks around it were considered to be related C_{12} compounds. The 2,2'-diketodicyclohexyl was separated from the reaction mixture for C,H and O analysis and molecular weight determinations [Pascher, 1960]; the results are recorded in Table III.6 along with the results of other similar determinations.

Gas chromatographic separation of the reaction mixture using the Silicone grease column and the Silicone rubber column gave similar results. However, infra-red spectral analyses of the peaks from these columns did not show the presence of unsaturation. Results of the C,H,O and molecular weight determinations [Pascher, 1960] of 2,2'-diketodicyclohexyl, separated using these two columns, are recorded in Table III.6.

Vacuum distillation.

The reaction mixture was distilled under vacuum and the distillate (B.P.121-123°/1-2mm; compare [Moore, 1961] B.P.116-117°/1mm) was collected as a very light pink coloured, viscous liquid ($\sim$5 ml). Its colour deepened at first and then changed to light yellow after standing for several days.

Gas chromatographic analysis of the distillate, using the Apiezon L column, showed the presence of three impurities in it. Assuming that the peak areas of 2,2'-diketodicyclohexyl and the impurities are proportional to their weight, the distillate was estimated to contain 75% of 2,2'-diketodicyclohexyl. The infra-red spectrum of the distillate was found to be quite similar to the infra-red spectrum of 2,2'-diketodicyclohexyl that had been separated gas chromatographically from the reaction

TABLE III.6

Analysis[a] of Dimer.

Determination	1	2	3	4	5
C %	74.2	73.3	75.8	73.5	74.6
H %	9.3	9.3	9.5	8.8	9.3
O %[b]	16.6	17.4	14.7	17.7	16.1
Mol.wt.	194	199	206	205[c]	205

1: Values required for 2,2' - diketodicyclohexyl.

2: Values for the dimer collected from the Apiezon L column.

3: Values for the dimer collected from the Silicone grease column.

4: Values for the dimer separated by vacumn distillation.

5: Values for the dimer collected from the Silicone rubber column.

a: All values are averages of two determinations, unless otherwise stated.

b: By difference.

c: Average of three determinations.

mixture using the Apiezon L column. However, it also indicated the presence of OH(bands at $3500cm^{-1}$, $1390cm^{-1}$, $1280\ cm^{-1}$ and $1125\ cm^{-1}$) and C=C (bands at $965cm^{-1}$ and $886\ cm^{-1}$).

In an attempt to get a purer sample of 2,2'- diketodicyclohexyl, it was redistilled under vacuum and the distillate was collected in three fractions (∽ 2,1.5 and 0.5 ml). The third fraction (∽0.5 ml) was found to contain the largest proportion of 2,2'-diketodicyclohexyl, which was estimated to be 83% by analyses on the Silicone grease and the Apiezon L columns. The results of the C,H,O and molecular weight determinations of this fraction are given in Table III.6.

It appears that the method used by Pascher [Pascher, 1960,1963] for molecular weight determinations gives results that are too high. Poor agreement between the experimental values and the values required for C,H and O for 2,2'-diketodicyclohexyl, separated by vacuum distillation (column 4), may be due to the impurities.

The gas chromatographic peak due to 2,2'-diketodicyclohexyl from the redistilled sample was found to correspond to the main dimer peak obtained by the separation of the reaction mixture on the Silcone grease and the Apiezon L columns.

It may be mentioned that fraction 2 of the redistilled diketone deposited prism shaped crystals after standing for about four weeks. The other two fractions remained viscous oils. The possibility of the formation of various stereoisomers of the diketone has been mentioned [Kharasch et al, 1948; Moore, 1951]. However, the configuration of the product obtained by these workers and by Plant [Plant, 1930] does not seem to have been determined though [Kharasch et al, 1948] it seems to have been assumed to be a mixture of the racemic and the meso forms of 2,2'-diketodicyclohexyl. In the present case both racemic and meso forms

are most likely to be formed. The first and the third fraction of the redistilled diketone were both found to be optically inactive. The crystals deposited in fraction 2 were separated mechanically and their solution in carbon tetrachloride was found to be optically inactive.

(ii) Dimeric radiolysis products.

The residue from a 9 ml sample of cyclohexanone (irradiated to $\sim 3\times10^{20}$ ev /ml), after removal of the contents that were volatile at room temperature (see sections II.C5.a. and II.C5.b), was about 0.2 ml of viscous liquid. A hot water bath was kept around the sample bearing trap and about 0.1 ml of the liquid was distilled into a liquid nitrogen cooled bulb. About 1 ml of degassed carbon tetrachloride (Spectro Grade) was distilled into the same bulb and the liquid nitrogen cooled bulb was sealed (referred to as 16.G hereafter).

About 1 ml of degassed carbon tetrachloride (Spectro Grade) was then distilled into the main trap containing the residual liquid and after shaking it very well the resulting solution was poured into an attached glass bulb, out of contact with air. Carbon tetrachloride was then distilled back into the main trap and was poured into the glass bulb again after shaking, and this process was repeated a few times. During this period about 10 mm pressure of purified nitrogen was maintained in the system to avoid vigorous frothing of the carbon tetrachloride. The bulb (hereafter referred to as 16.H) was finally cooled (-196°C) and the solution was sealed in it after pumping away most of the nitrogen.

Infra-red spectra of the two solutions, 16.G and 16.H, indicated the presence of C=C (bands at 1625 cm^{-1}, 985cm^{-1} and 886 cm^{-1}), and OH (bands at 3400-3600 cm^{-1}, 1390 cm^{-1}, 1280cm^{-1}, 1125$cm^{-1}$and 1032 cm^{-1}). These spectra resembled each other very much and showed an overall

resemblance with the infra-red spectrum of 2,2'-diketodicyclohexyl, thus indicating that 2,2'-diketodicyclohexyl and related C_{12} compounds are present in solutions 16.G and 16.H. However, it is not possible to say whether the C=C and OH frequencies in their spectra originated from C_6, C_{12} or polymeric compounds.

(iii) Products separated gas chromatographically.

On separation of the radiolysed cyclohexanone using the Apiezon L column only one gas chromatographic peak was obtained, well after the cyclohexanone peak. The retention time of this peak agreed with the retention time of 2,2'-diketodicyclohexyl.

On separation of the radiolysed cyclohexanone using the Silicone grease column five peaks (two of which were doublets) were obtained in the same region where the peaks corresponding to 2,2'-diketodicyclohexyl and related compounds (see section c(i)above) had been obtained. The retention time of the largest peak agreed with the retention time of 2,2'-diketodicyclohexyl.

Collection of the products corresponding to the various dimer peaks, using the Apiezon L column and the Silicone grease column (and also the Silicone rubber column) followed by their infra-red spectral analyses showed that their infra-red spectra were similar to the spectra of 2,2'-diketodicyclohexyl and related compounds that had been separated from the same columns (mentioned in c(i) above).

The gas chromatogrphic peak in question, using the Apiezon L column was therefore taken to contain 2,2'-diketodicyclohexyl and some other related C_{12} products. The four smaller peaks from the Silicone grease column were also considered to be due to similar C_{12} products.

On the basis of the above mentioned work no conclusions can be drawn about the configuration of the C_{12} products obtained. In most cases the physical properties of the meso form and the racemic modification of the same optically active compound are sufficiently different that such substances have come to be known as "physical isomers" [Hückel, 1955]. Therefore the separation of the two forms by gas chromatography should be considered as possible. The possibility of the separation of racemic modifications into their optically active forms, by gas chromatography, has also been recently indicated [Casanova and Corey, 1961].

It may also be mentioned that the presence or absence of either C=C or OH in any of these products could not be established on the basis of the above mentioned work.

2. Quantitative Results.

a. Fragmentation products.

(i) -196° and -70° fractions.

The G values of these two fractions of the gaseous products are given in Figure III.1, as a function of the absorbed dose.

The G value for the -196° fraction (Fig. III.1.A) appears to be constant with dose and dose rate, in the region investigated. The extrapolated value for zero dose for this fraction is $G_i(-196^{\circ}) = 1.23$.

The G value for the -70° fraction (Fig. III.1.B) also appears to be constant with dose and dose rate, in the region investigated. The values obtained for the lower dose samples are less reliable than the values obtained for the higher dose ones. The extrapolated value for zero dose for this fraction is $G_i(-70^{\circ}) = 0.38$.

(ii) Hydrogen and carbon monoxide.

The G values of hydrogen and carbon monoxide are shown in

FIGURE III.1

Fragmentation Products

○ Dose rate $\sim$ 6 x 10^{18} ev /ml hr; cyclohexanone measured out of contact with air.

□ Dose rate $\sim$ 8 x 10^{17} ev /ml hr; cyclohexanone measured out of contact with air.

△ Dose rate $\sim$ 8 x 10^{17} ev/ ml hr; cyclohexanone measured with pipette.

A: -196^{o} fraction

B: -70^{o} fraction

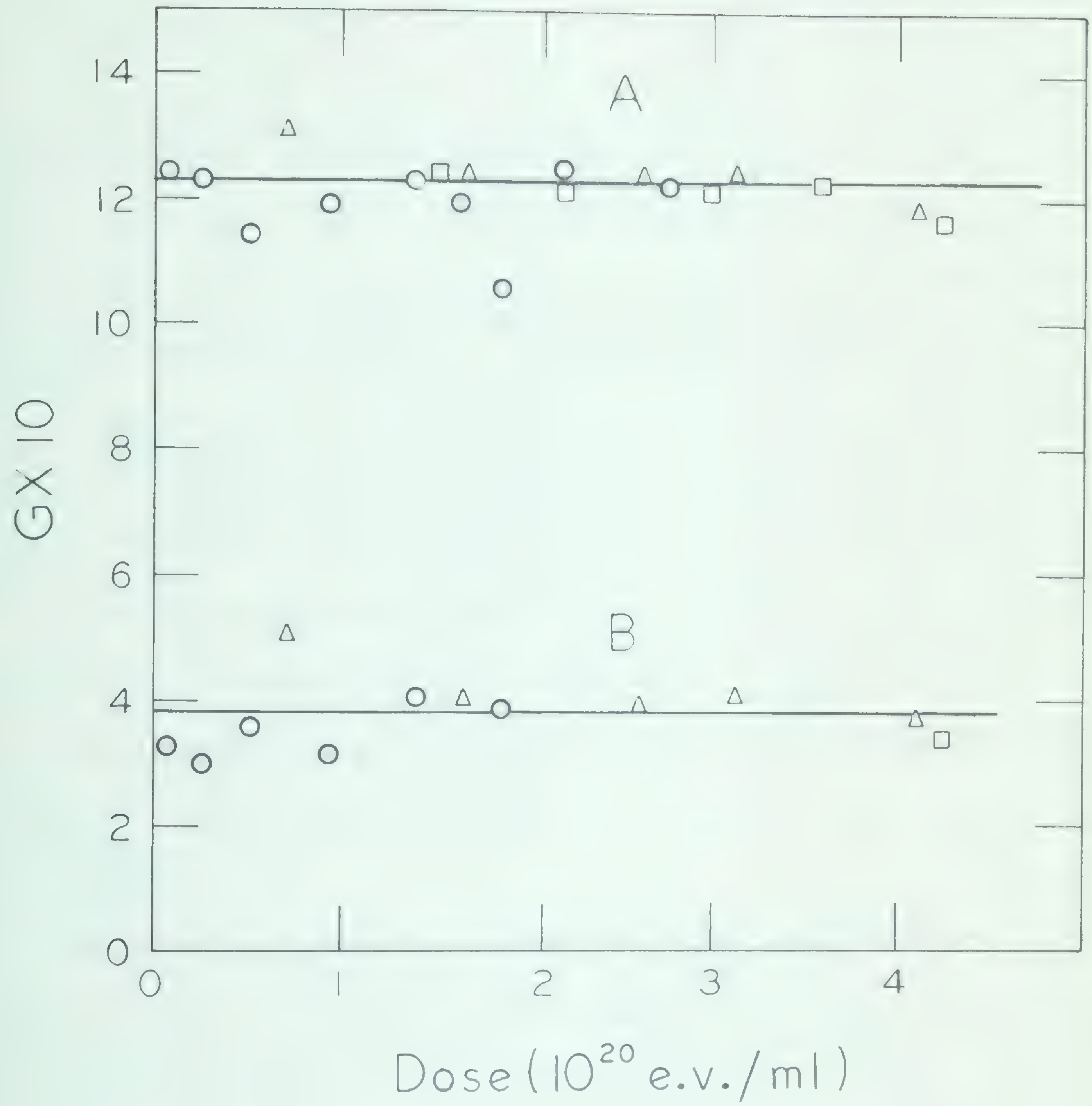

14
12
10
8
6
4
2
0
A
B
GX 10
0
1
2
3
4
Dose (10^{20} e.v./ml)

Figure III.2, as a function of the absorbed dose. The G value of hydrogen seems to decrease slightly with dose whereas the G value of carbon monoxide seems to be constant.

The G values for both these products could be calculated in two ways. Either each of these could be calculated directly (G_{dir}) from their respective gas chromatographic peak using appropriate calibrations (Figs. III.3 & III.4) or, one product could be obtained from its gas chromatographic peak (G_{dir}) and the other could be obtained by subtracting G_{dir} from G(-196°) for that particular sample, (G_{dif}). The values given in Figure III.2 are averages for G_{dir} and G_{dif} for each sample. The average difference between G_{dir} and G_{dif} was 1.3% for hydrogen and 2.0% for carbon monoxide.

The extrapolated value for zero dose for hydrogen is, G_i (H_2) = 0.76 and that for carbon monoxide is, G_i (CO) = 0.48.

The calibrations for hydrogen and carbon monoxide are shown in Figures III.3 and III.4 respectively.

(iii) Ethylene.

The G value of ethylene is shown in Figure III.5.B, as a function of dose. It seems to decrease slowly with increasing dose. The extrapolated value for zero dose is, G_i (C_2H_4) = 0.12.

The calibration for ethylene is shown in Figure III.6.

(iv) Ethane.

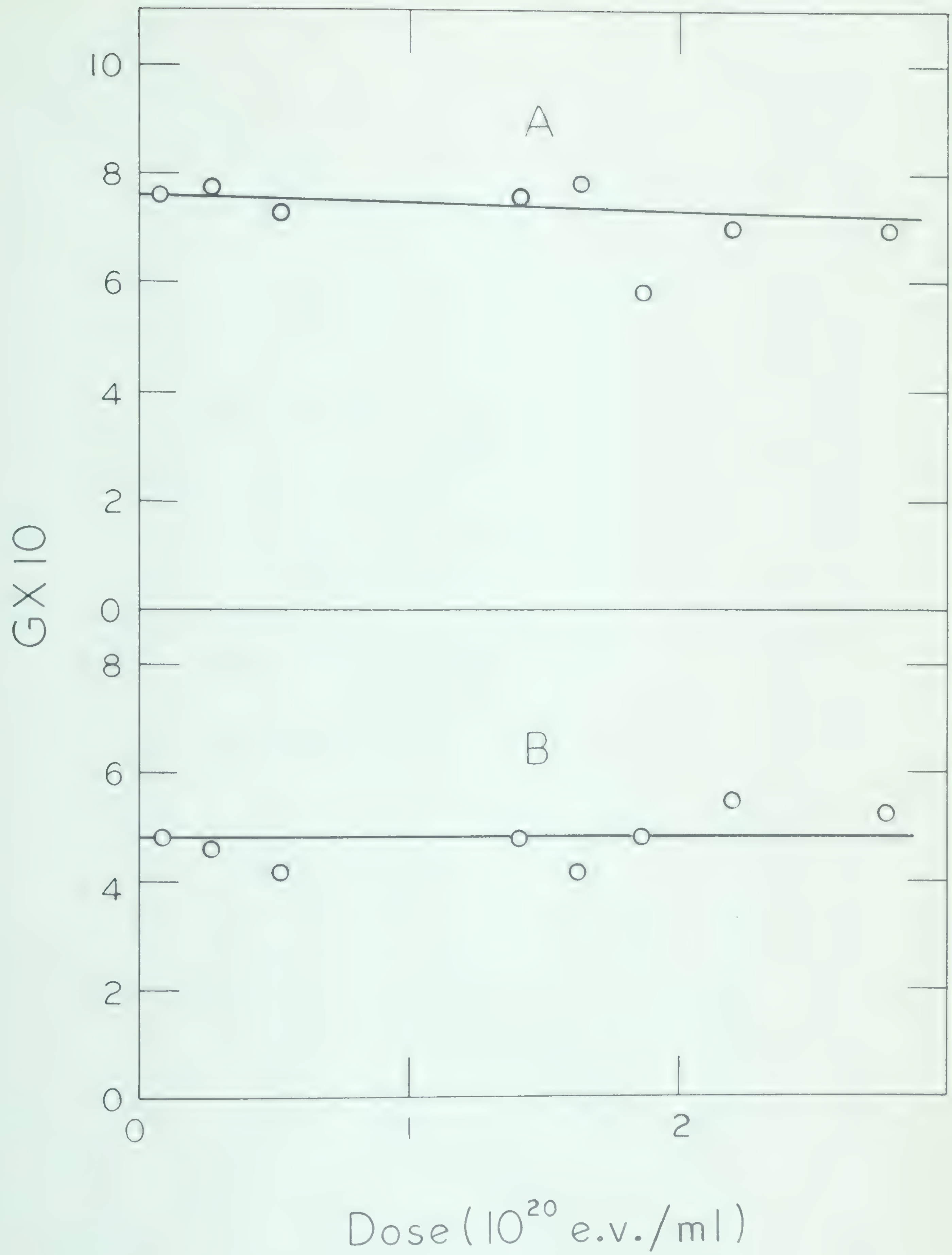
The G value of ethane is shown in Figure III. 7.E. The gas chromatographic peak corresponding to ethane was very small and could be measured only in three of the high dose samples. However, it was visible in most of the lower dose samples also. Its G value is = 0.005, in the dose range 1.6-2.8 (10^{20} ev/ ml).

FIGURE III.2

Hydrogen and Carbon Monoxide

A: Hydrogen

B: Carbon monoxide

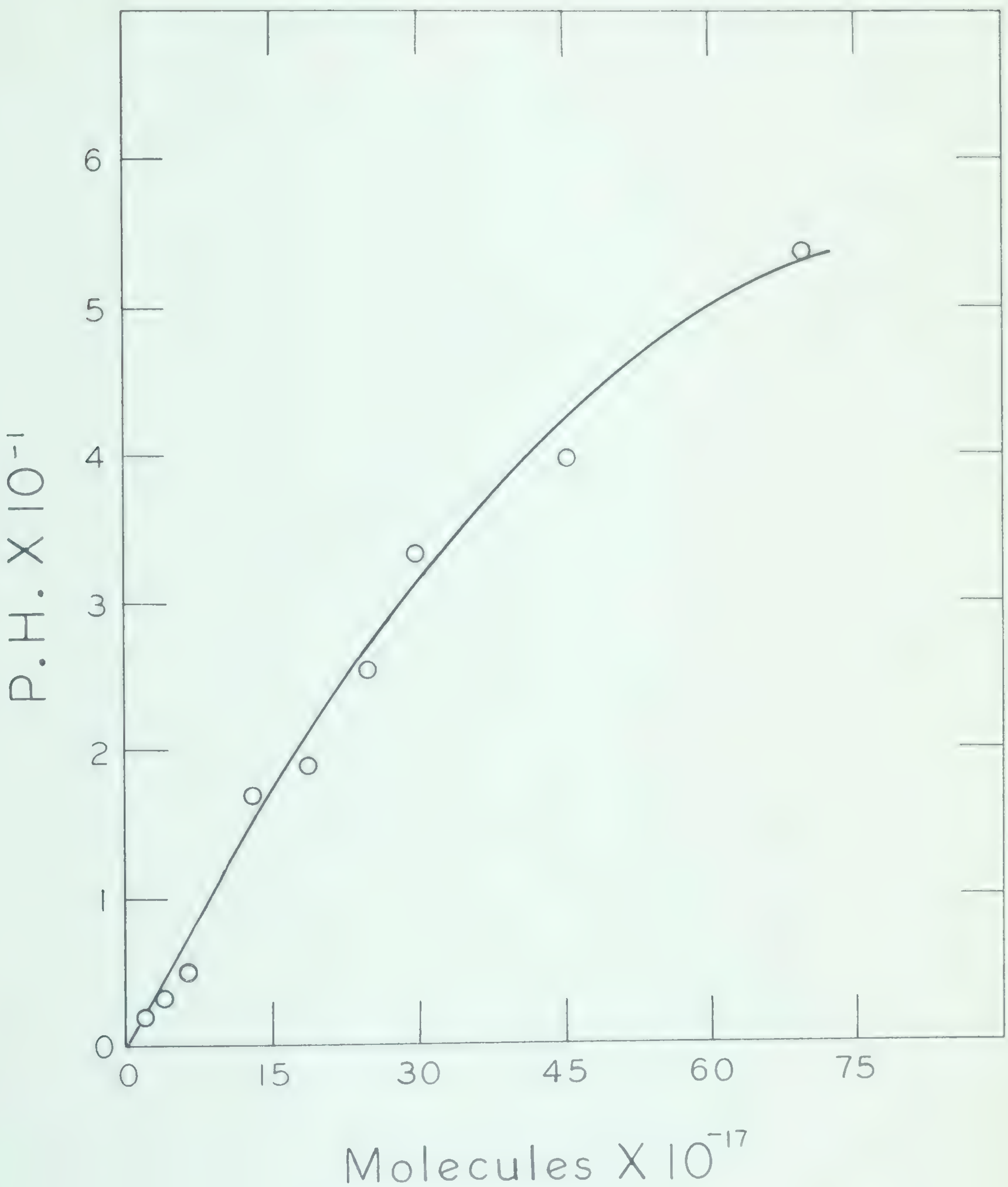


10
8
6
4
2
0
8
6
4
2
0
GX10
A
B
0
1
2
Dose (10^20 e.v./ml)

FIGURE III.3

Hydrogen Calibration

P.H. = Peak height; [Unit, 1/32"].

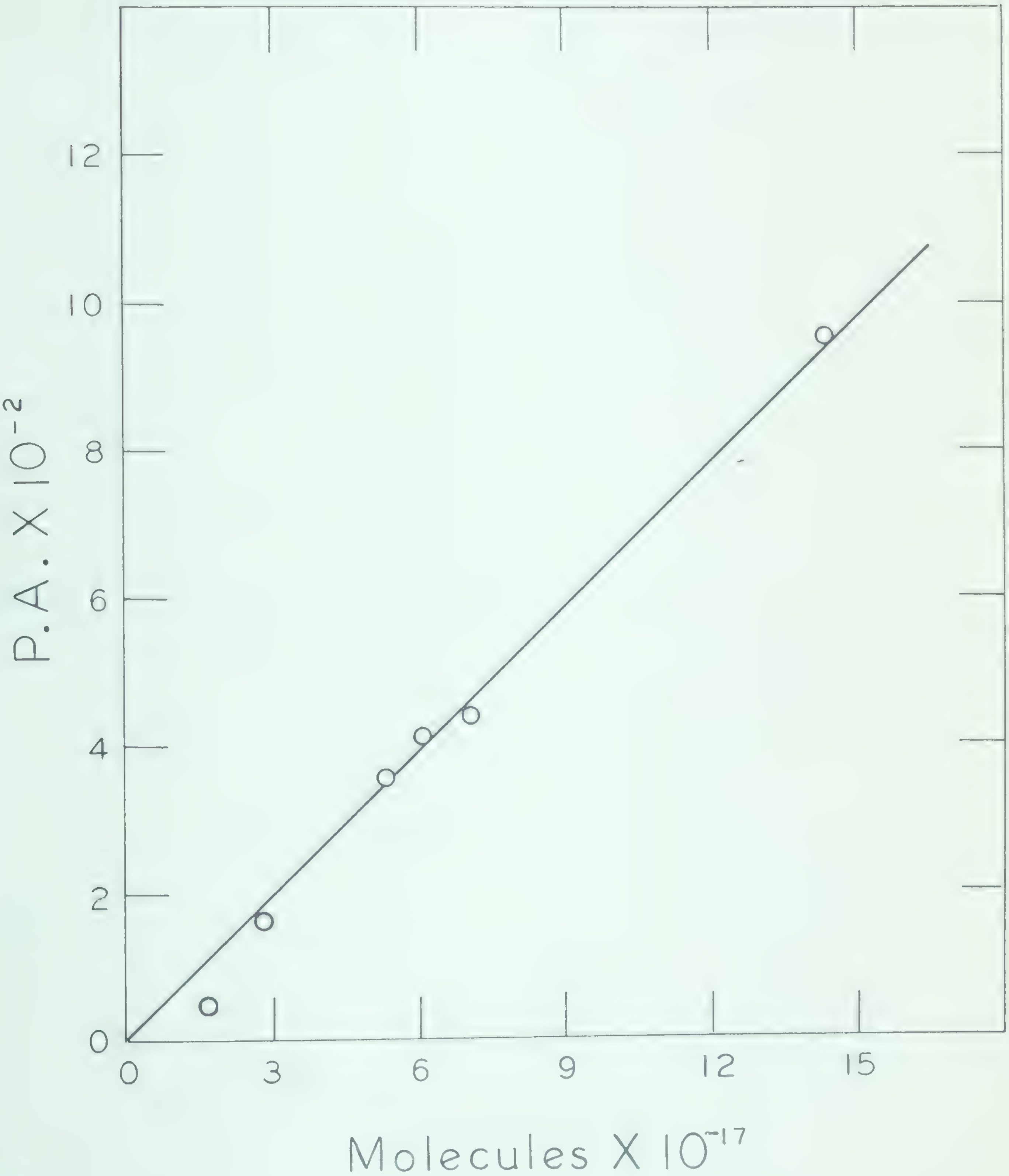


P.H. X 10^-1
0
1
2
3
4
5
6
0
15
30
45
60
75
Molecules X 10^-17

FIGURE III.4.

Carbon Monoxide Calibration

P.A. = Peak area; [Unit, (1/32)"].



P.A. X 10⁻²
12
10
8
6
4
2
0
0
3
6
9
12
15
Molecules X 10⁻¹⁷

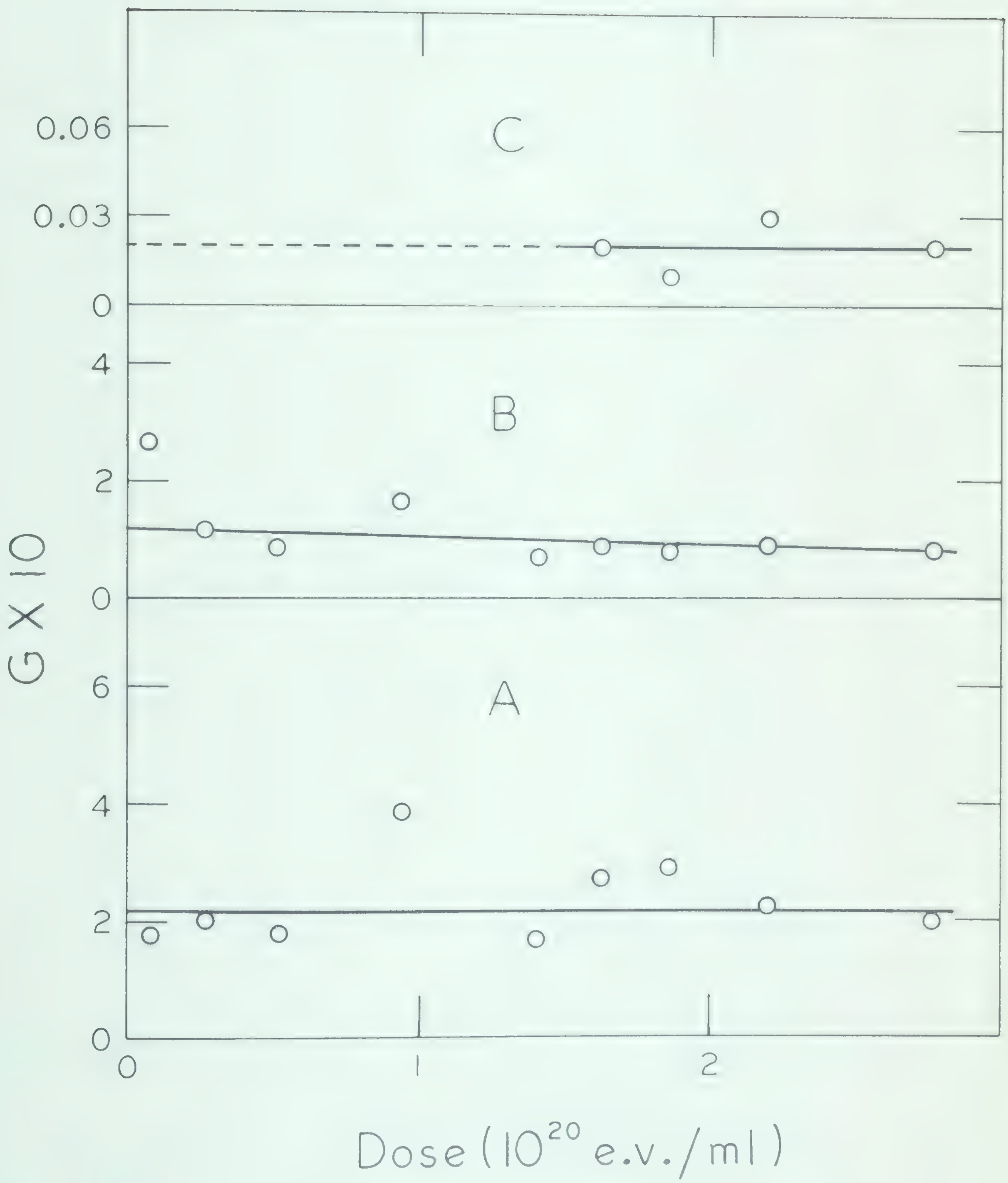
FIGURE III.5

Yields of 1-Pentene, Ethylene and 1-Butene.

A: 1-Pentene

B: Ethylene

C: 1-Butene

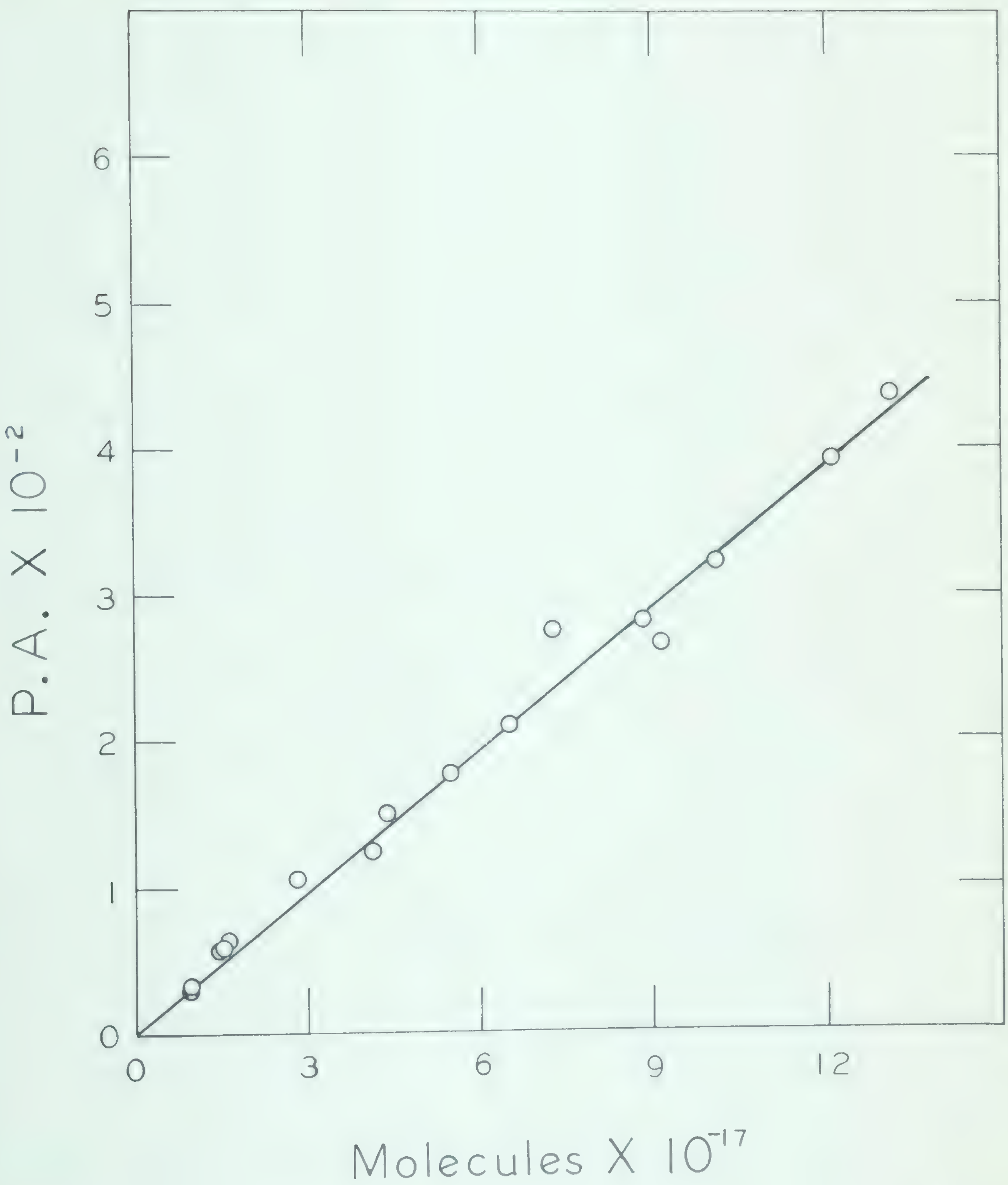


0.06
0.03
0
4
2
0
6
4
2
0
C
B
A
G X 10
0
1
2
Dose (10^{20} e.v./ml)

FIGURE III.6.

Ethylene Calibration

P.A. = Peak area; [Unit, $(1/32")^2$]



P. A. X 10^{-2}
0
1
2
3
4
5
6
0
3
6
9
12
Molecules X 10^{-17}

FIGURE III.7.

Some Fragmentation Products

A: Cyclopropane

B: Propylene

C: n-Pentane

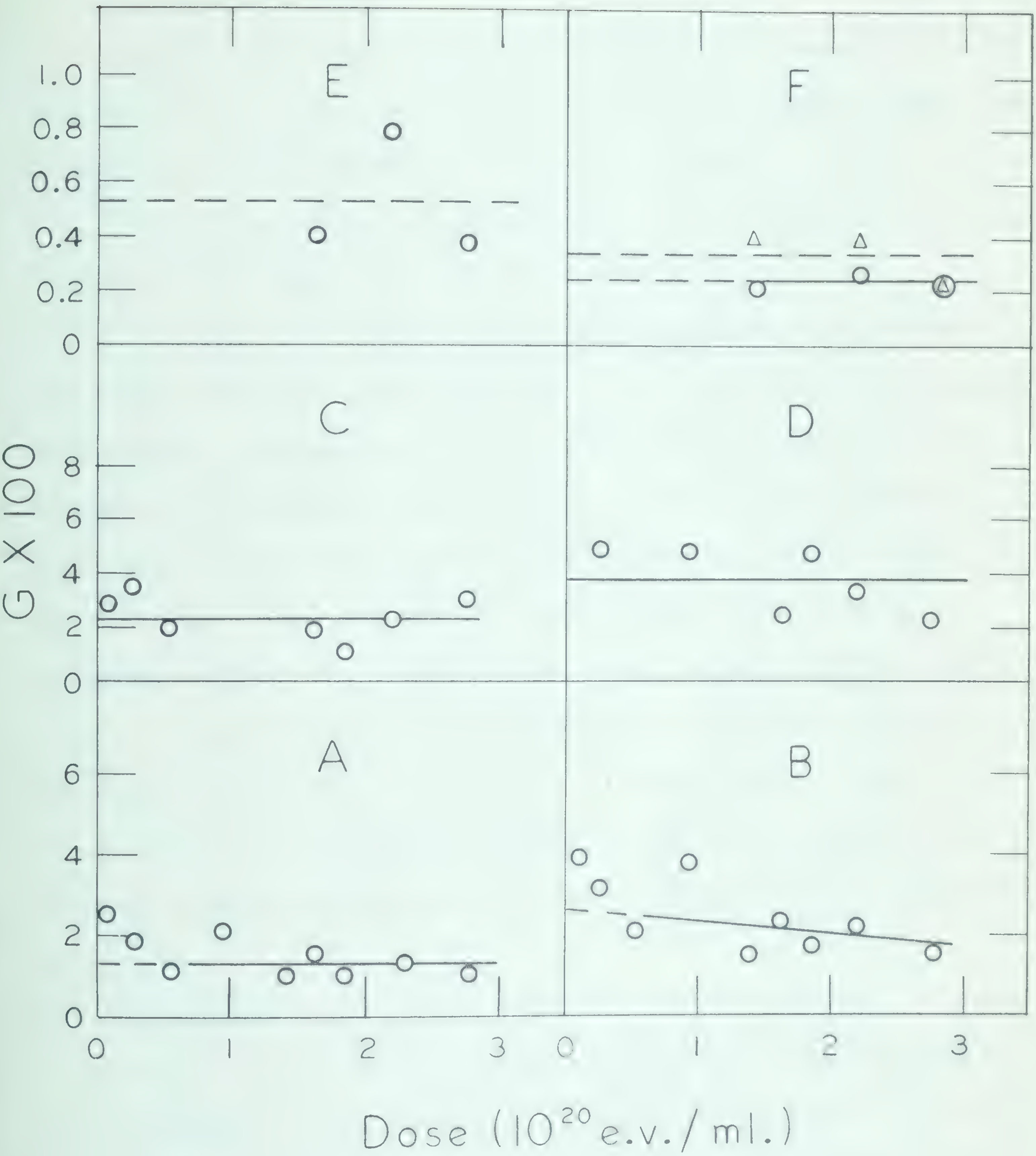
D: Cyclopentane

E: Ethane

F: Propane and Acetylene

○ Propane

△ Acetylene


E
F
C
D
A
B
G X 100
1.0
0.8
0.6
0.4
0.2
0
8
6
4
2
0
6
4
2
0
0
1
2
3
0
1
2
3
Dose (10^{20} e.v./ml.)

Ethylene was used as an internal standard for ethane and the calibration factor for ethane was calculated to be 1.02.

(v) Acetylene and propane

Acetylene and propane could be measured only for three of the higher dose samples though they were visible in the low dose samples also. The G value for acetylene is about 0.003 in the region 1.6 to 2.8 (10^{20} ev/ ml and is shown in Figure III.7.F. The G value for propane is also shown in Figure III.7.F and is about 0.002.

It was found that when acetylene and propane are both present in very small quantities, their peaks are resolved just enough for separate measurements. During analysis of the -70° fraction, these two peaks appeared to be of similar size. However, in larger amounts during calibrations, they were found to give a single peak. The calibration for acetylene and propane was done using a gaseous mixture which contained acetylene and propane in the ratio (molar) 6.93/6.05, and is shown in Figure III.8.C. It was assumed that the relative peak areas of acetylene and propane are proportional to their weight. Figure III.8.C. was used along with appropriate scaling factors obtained on the basis of the above mentioned assumption, to calculate the G values of acetylene and propane.

(vi) Cyclopropane

The variation of the G value of cyclopropane with the absorbed dose of cyclohexanone is shown in Figure III. 7.A. It is probably constant with dose with $G_i = 0.013$. The calibration for cyclopropane is shown in Figure III.9.B.

(vii) Propylene

The variation of the G value for propylene with dose is shown in

FIGURE III.8.

Hydrocarbon Calibrations

P.A. = Peak area; [Unit, $(1/32")^2$]

A: n-Butane

B: 1-Butene

C: Acetylene + Propane

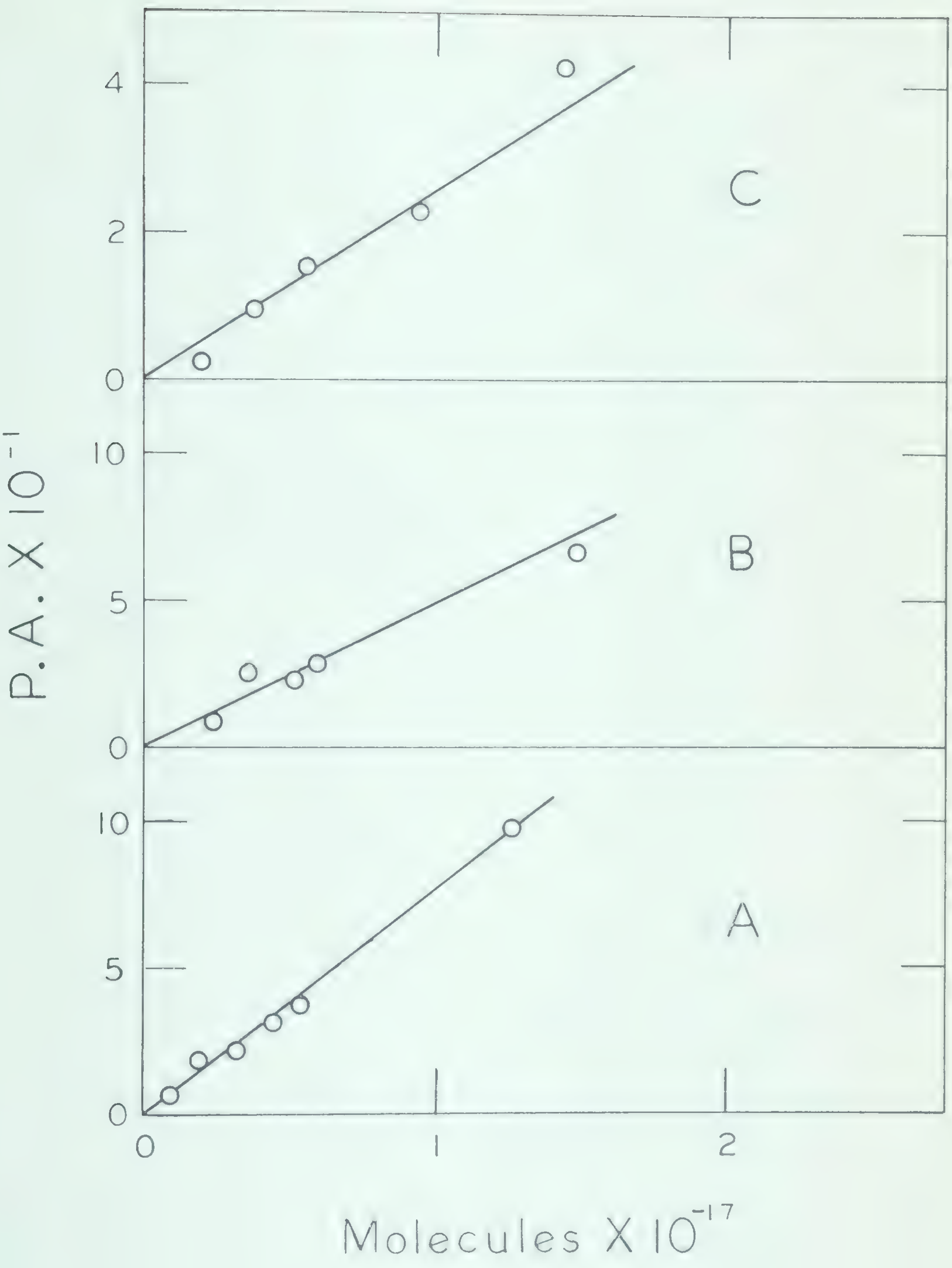

4
2
0
10
5
0
10
5
0
C
B
A
P.A. X 10^{-1}
0
1
2
Molecules X 10^{-17}

FIGURE III.9

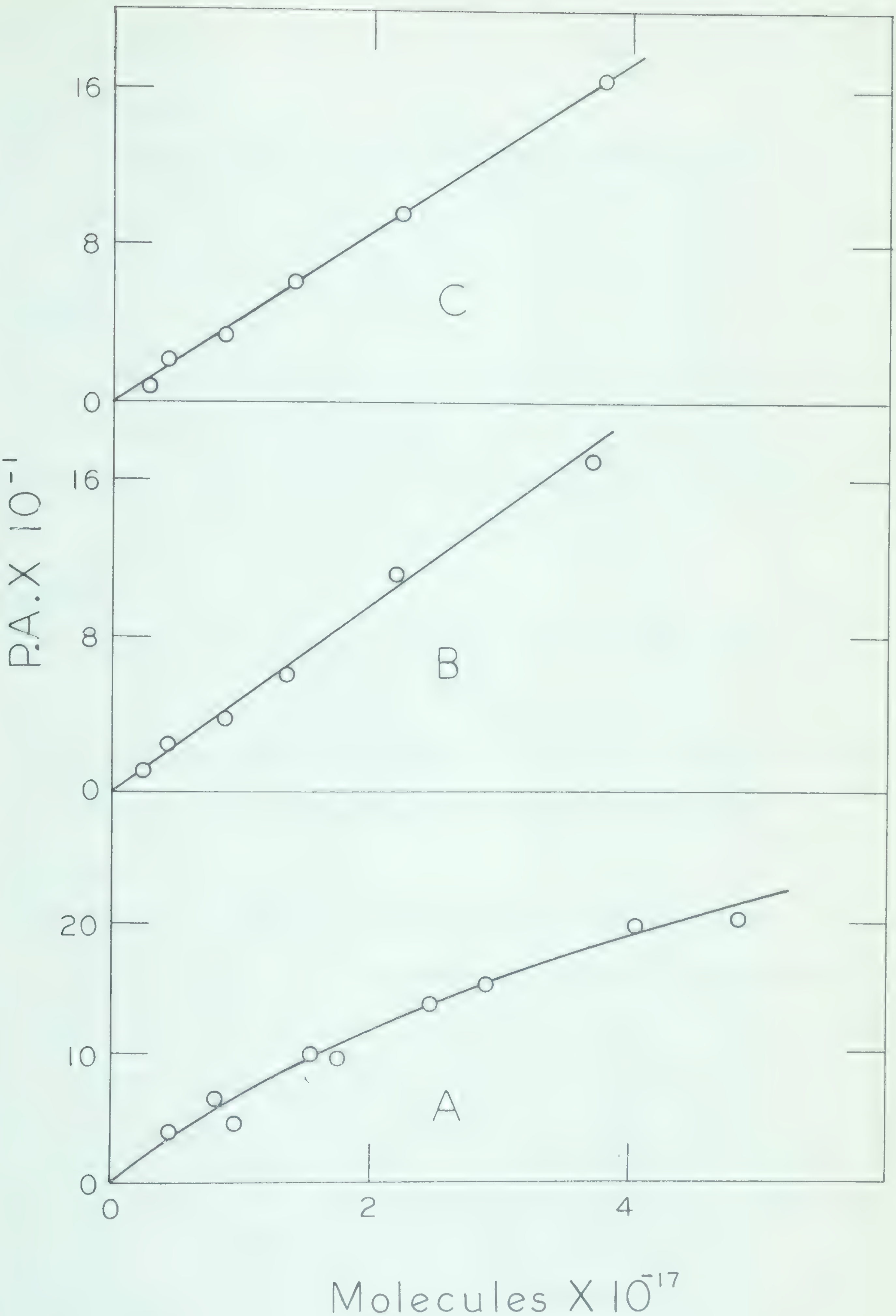
Hydrocarbon Calibrations

P.A. = Peak area; [Unit, $(1/32'')^2$]

A: n-Pentane

B: Propylene

C: Cyclopropane



P.A. X 10^{-1}
16
8
0
C
16
8
0
B
20
10
0
A
0
2
4
Molecules X 10^{-17}

Figure III.7.B. It seems to decrease with dose and G_i is equal to 0.026. The calibration for propylene is shown in Figure III.9.A.

(viii) Methyl acetylene.

Methyl acetylene could be seen as a minor product in most of the samples. For the sample with a dose of 2.2×10^{20} ev/ml, its G value was estimated to be $\sim$ 0.002.

(ix) n-Butane.

Normal butane could be seen as a minor product in most of the samples. For the sample with dose equal to 2.8×10^{20} ev./ml, its G value was 0.0008. The calibration for n-butane is shown in Figure III. 8.A.

(x) 1-Butene.

The variation of the G value of 1-butene with dose is shown in Figure III.5.C. The G value for the dose region 1.4 to 2.8 (10^{20} ev./ml) is about 0.002. It could be seen in the lower dose samples also. The calibration for 1-butene is shown in Figure III.8.B.

(xi) n-Pentane

The G value of n-pentane is given in Figure III.7.C, as a function of dose. It seems to be constant with dose and the extrapolated value for zero dose is, $G_i = 0.023$. These values have been obtained by analyses of the - 70^o fraction on both, the Silica gel column and the di-n-decyl phthalate column, with the help of the calibrations shown in Figures III.9.A and III.10 (the Silica gel column separates 1-pentene from cyclopentane and n-pentane whereas the di-n-decyl phthalate column gives a combined peak for 1-pentene + n-pentane and another for cyclopentane).

FIGURE III.10

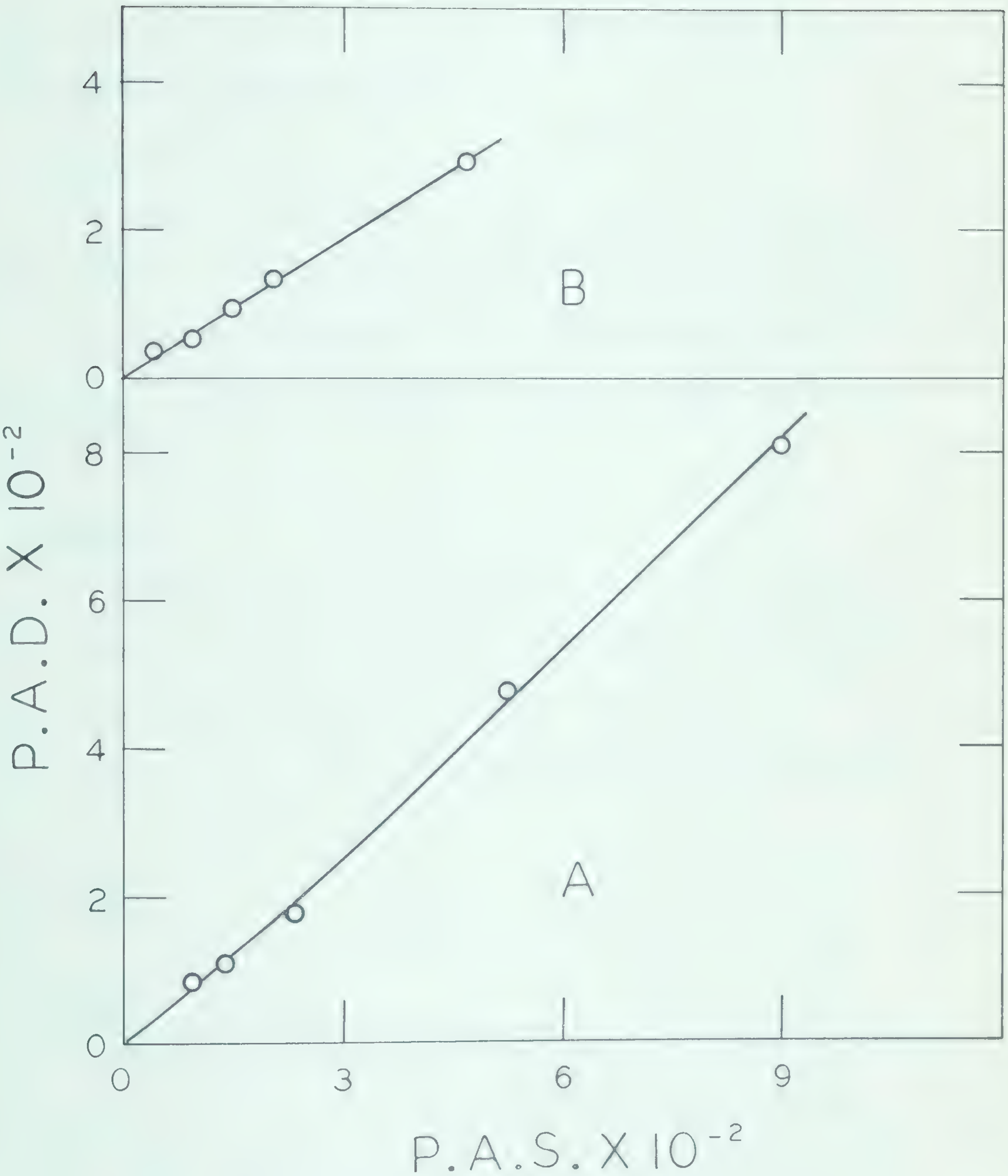
n-Pentane and 1-Pentene Calibrations

P.A.D. = Peak area on the di-n-decyl phthalate column; [Unit, $(1/32'')^2$]

P.A.S. = Peak area on the Silica gel column; [Unit, $(1/32'')^2$]

A: 1-Pentene

B: n-Pentane



4
2
0
B
8
6
4
2
0
A
0
3
6
9
P.A.D. X 10⁻²
P.A.S. X 10⁻²

(xii) Cyclopentane.

The variation of the G value of cyclopentane with dose is shown in Figure III. 7.D and is probably independent of dose (G_i = 0.04). Several sets of calibrations were done for cyclopentane on the di-n-decyl phthalate column. These are shown in Figure III. 11.B to show the degree of reproducibility.

(xiii). 1-Pentene.

The G value of 1-pentene is shown in Figure III.5.A, as a function of dose. It appears to be independent of dose with G_i = 0.22. Several sets of calibrations were done for 1-pentene on the Silica gel column. These are shown in Figure III. 11.A to show the degree of reproducibility.

(xiv) 2-Pentene.

This product could be measured only in the two highest dose samples, though it could be seen in most of them. The average G value for these two samples is equal to 0.004. The calibration factor, using ethylene as an internal standard, was obtained, and was found to be equal to 2.1.

b. C_6 products.

(i) 5-Hexenal.

The variation of the yield of 5-hexenal with dose is shown in Figure III.12.B, and is seen to decrease with increasing dose, with G_i = 0.85. The calibration curve obtained for 5-hexen-2-one and shown in Figure III. 13.A. was used to calculate the G values for 5-hexenal.

Similar G values for 5-hexenal were also obtained for some samples using the di-n-decyl phthalate column. However, the hexenal peak was very broad and seemed to be less reliable than the hexenal

FIGURE III.11.

Cyclopentane and 1-Pentene Calibrations.

P.A. = Peak area; [Unit, $(1/32")^2$].

△ Set 1

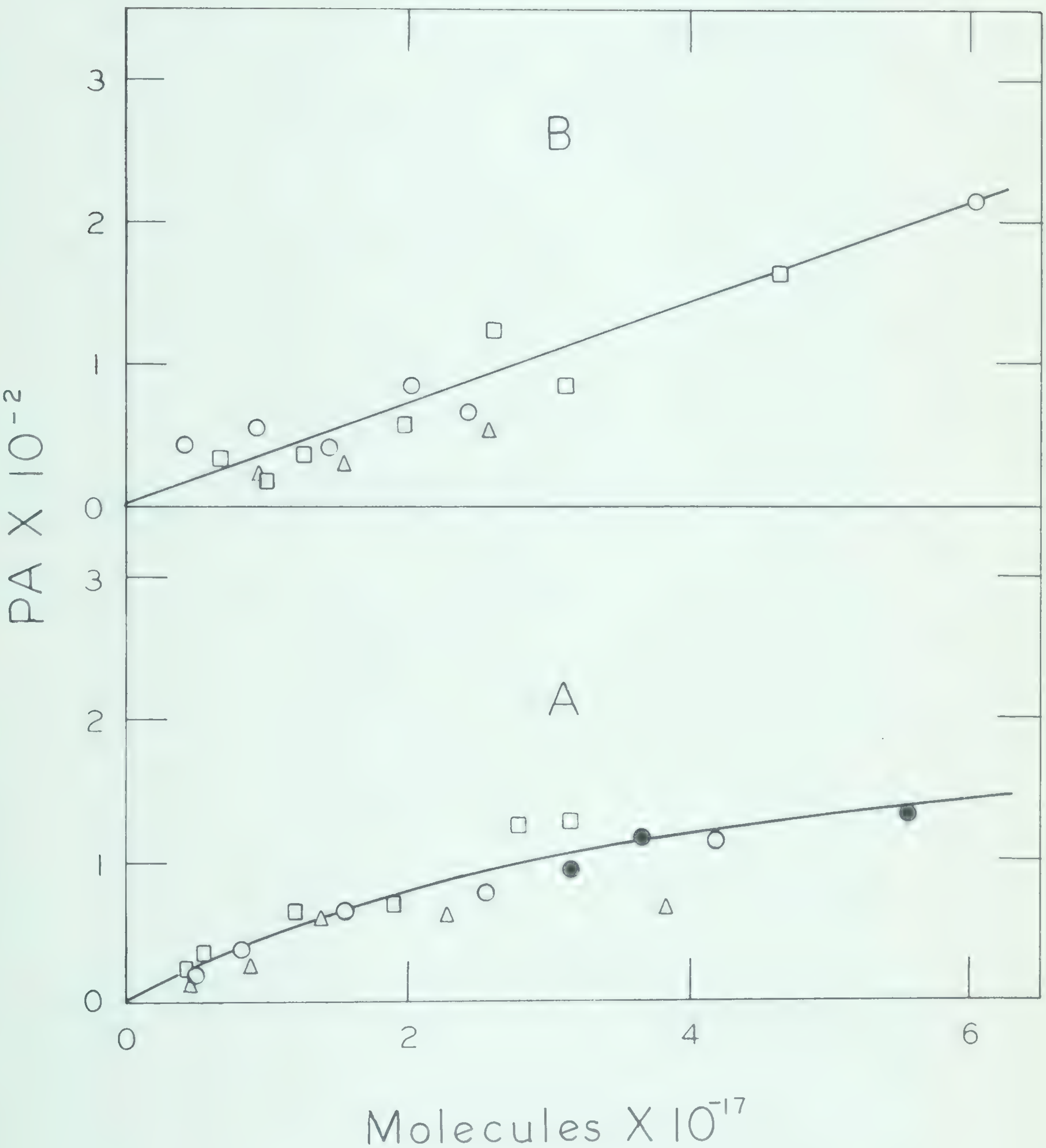
○ Set 2

□ Set 3

⊕ Set 4

A: 1-Pentene

B: Cyclopentane



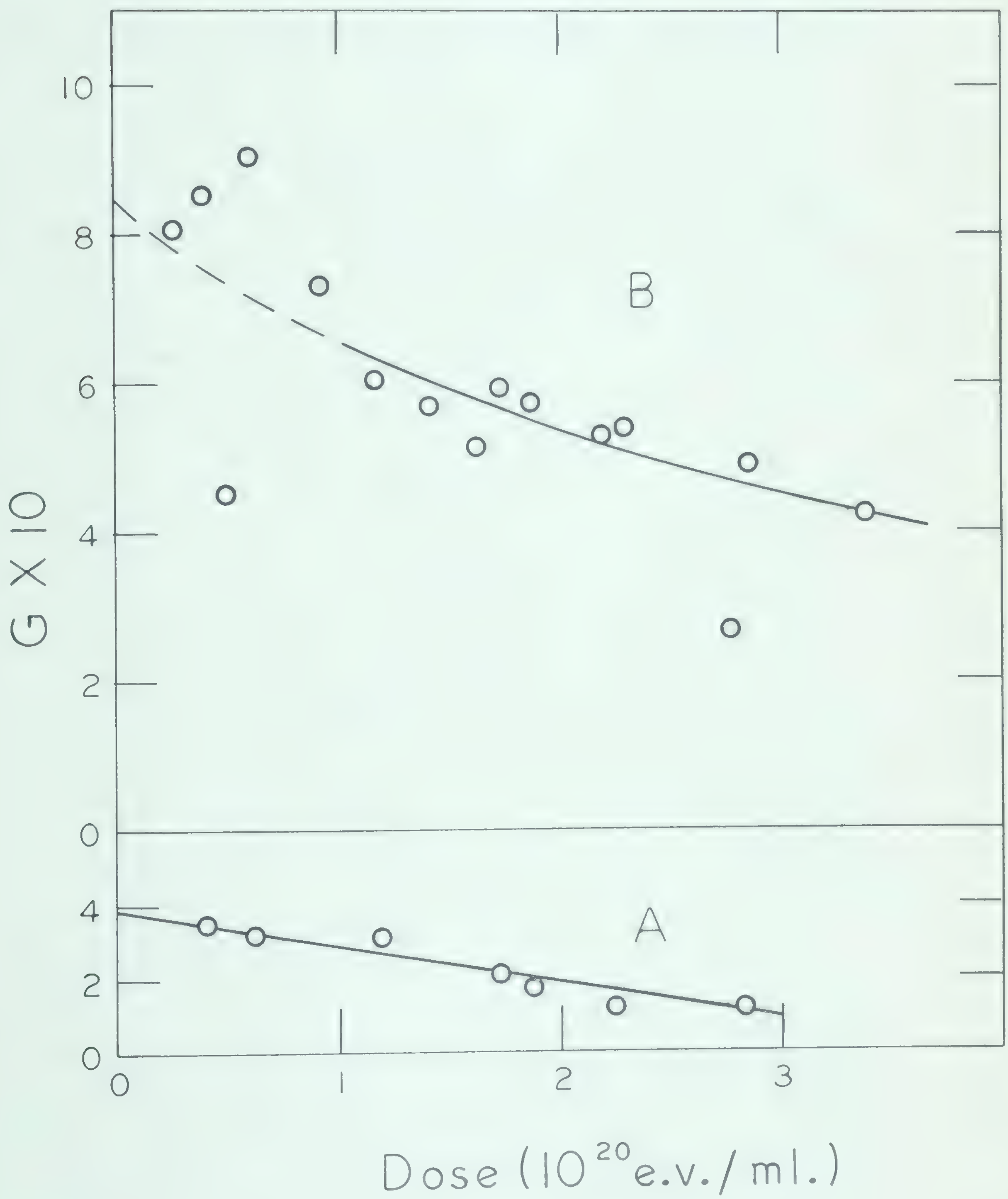
B
A
PA X 10^{-2}
0
1
2
3
0
1
2
3
0
2
4
6
Molecules X 10^{-17}

FIGURE III.12

Yields of Cyclohexenone and 5-Hexenal.

A: Cyclohexenone

B: 5-Hexenal



G X 10
10
8
6
4
2
0
4
2
0
0
1
2
3
B
A
Dose (10^{20} e.v./ml.)

FIGURE III.13

Cyclohexanol and 5-Hexen-2-one Calibrations.

A.R. = Area of the peak/ Area of cyclohexanone peak.

C.F. = Calibration factor

A: 5-Hexen-2-one

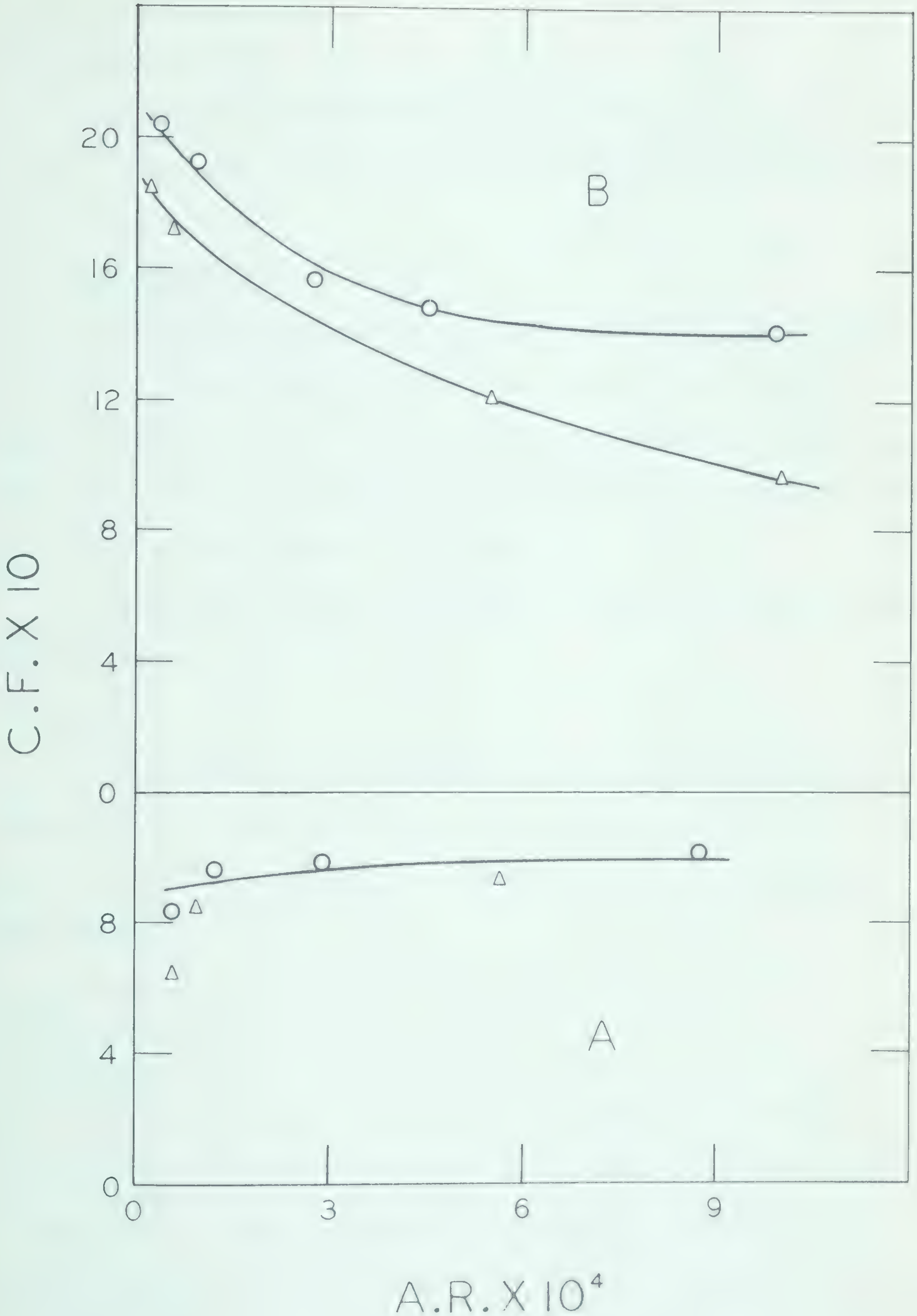
△ Set 1.

○ Set 2.

B: Cyclohexanol

○ Ucon column

△ Carbowax column



C.F. X 10
A.R. X 10^4
B
A
20
16
12
8
4
0
8
4
0
0
3
6
9

peak on the Ucon column, so the use of the di-n-decyl phthalate column was discontinued.

(ii) Cyclohexenone.

The yield of cyclohexenone decreases with dose (Fig. III.12.A) with $G_i \backsim 0.4$. The calibration factor for cyclohexenone was found to be 1.8 ± 0.9.

(iii) Cyclohexanol.

The results obtained for cyclohexanol are not too satisfactory, as shown in Figure III.14.B. The main reason for the scatter of the points is that a suitable column could not be found which would give a good separation of cyclohexanol from a large excess of cyclohexanone. The initial G value appears to be about 0.5.

The calibrations for cyclohexanol on the two columns used are shown in Figure III.13.B.

(iv) U.I.

The decrease of this unidentified impurity with dose is shown in Figure III.14.A. The calibration curve obtained for 5-hexen-2-one (Fig. III. 13.A.) was used, as a near approximation, to calculate these values.

c. C_{12} products.

(i) Total dimer.

The variation with dose of G (total dimer) as estimated by analyses on the Silicone grease and the Apiezon L columns is shown in Figure III.15. The G values for zero dose appear to be 1.53 (Silicone grease column) and 0.76 (Apiezon L column). In both cases the G value decreases with dose, though the decrease is more pronounced for the values from the Silicone grease column. The calibrations used for

FIGURE III.14.

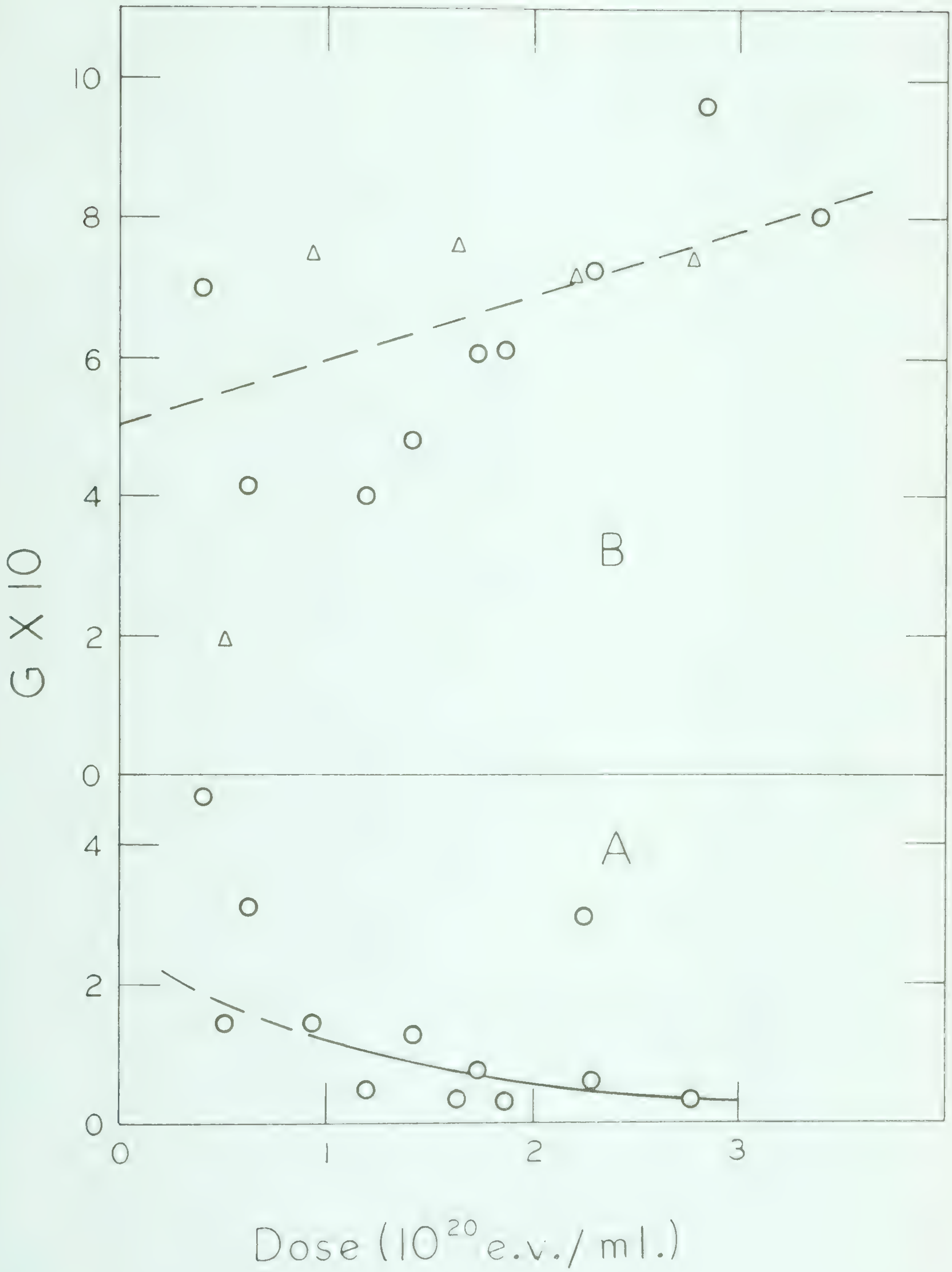
Cyclohexanol and U.I.

A: G(consumption) of U.I.

B: Cyclohexanol

○ Average of values from the Ucon and the Carbowax Columns.

△ Values from the Ucon column.

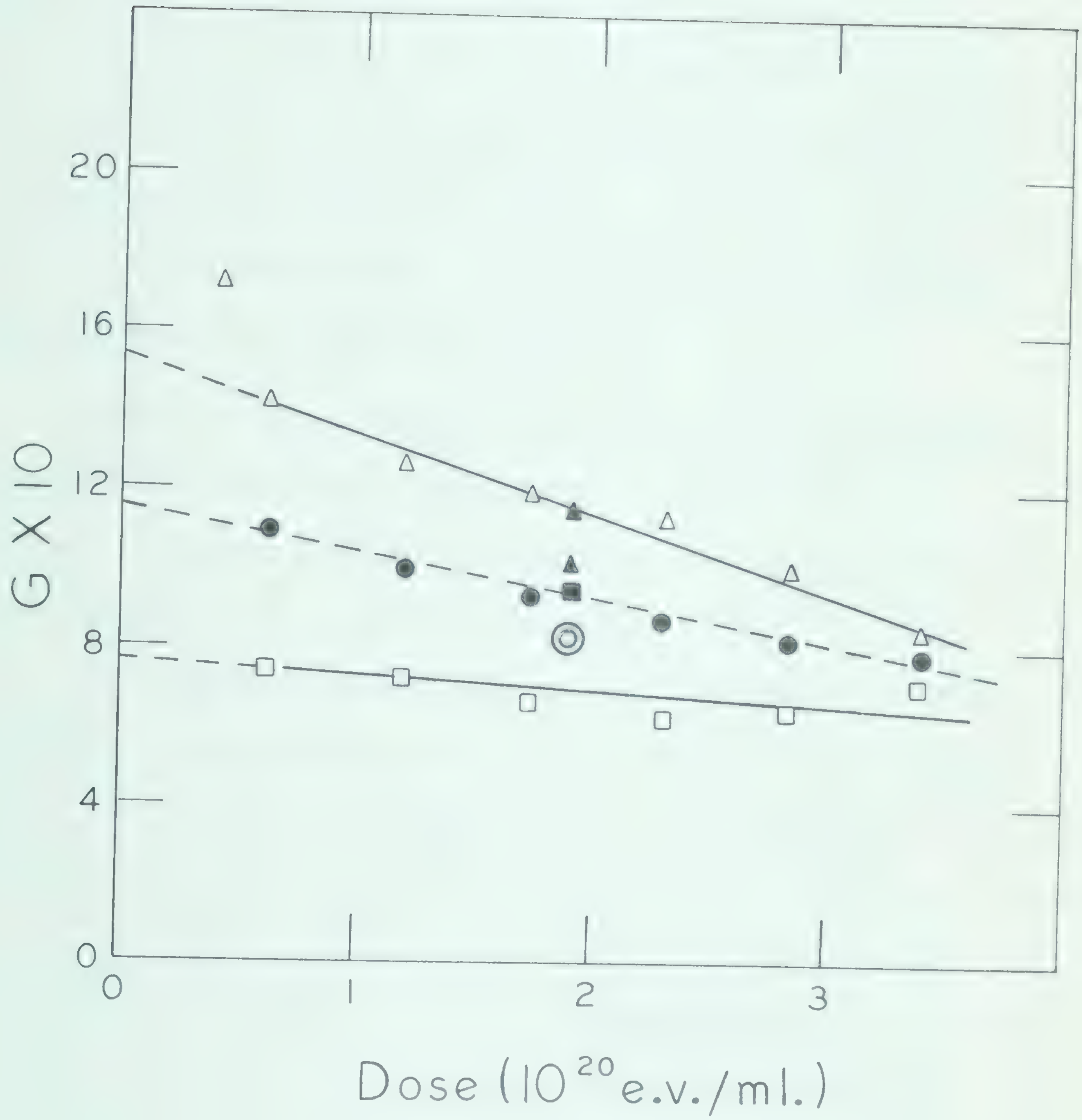


G X 10
10
8
6
4
2
0
4
2
0
0
1
2
3
B
A
Dose (10^20 e.v./ ml.)

FIGURE III.15.

Yield of Total Dimer.

△	Values from the Silicone grease column (Jan.'62).
□	Values from the Apiezon L column (Jan.'62).
●	Average of the values from the two columns (Jan.'62).
◎	Values for two samples from the Apiezon L column (March,'63).
▲	Values for two samples from the Silicone greas column (March, '63).
■	Average of the four values (March,'63



20
16
12
8
4
0
G X 10
0
1
2
3
Dose (10^{20} e.v./ml.)

calculating these values are shown in Figure III. 16.

It is difficult to ascertain the significance of the difference in the G values from the two columns. It is possible that some dimeric products might be giving measurable peaks on the Silicone grease column while the same products may not give measurable peaks on the Apiezon L column, under the conditions used. This possibility cannot be put to test without the availability of a large number of C_{12} compounds which could be considered as possible products of radiolysis of cyclohexanone, (and also some possible products larger than C_6 but smaller than, say, C_{15}).

Because it is not known which column gave the more accurate values of G (total dimer), the averages of the values obtained from the two columns are considered to be more trustworthy - with the knowledge that these might be wrong by about 30%.

The calibrations shown in Figure III.16 were done in August, 1963, whereas the samples referred to in Figure III.15 (open triangles and squares) were analysed in January, 1963. Calibrations were done at that time too, but the 2,2'-diketodicyclohexyl for the purpose was obtained by gas chromatographic separation. During later work, in May, 1963, it became evident that large and undetermined amounts of impurities were being collected with 2,2'- diketodicyclohexyl, upon gas chromatographic separation (calibration factors kept changing with each batch of 2,2'-diketodicyclohexyl collected). It was therefore decided to obtain 2,2'-diketodicyclohexyl by vacuum distillation of the preparation reaction mixture, for calibrations.

The values for two samples of irradiated cyclohexanone that were analysed in March, 1963, as a check on the previous work, are also given

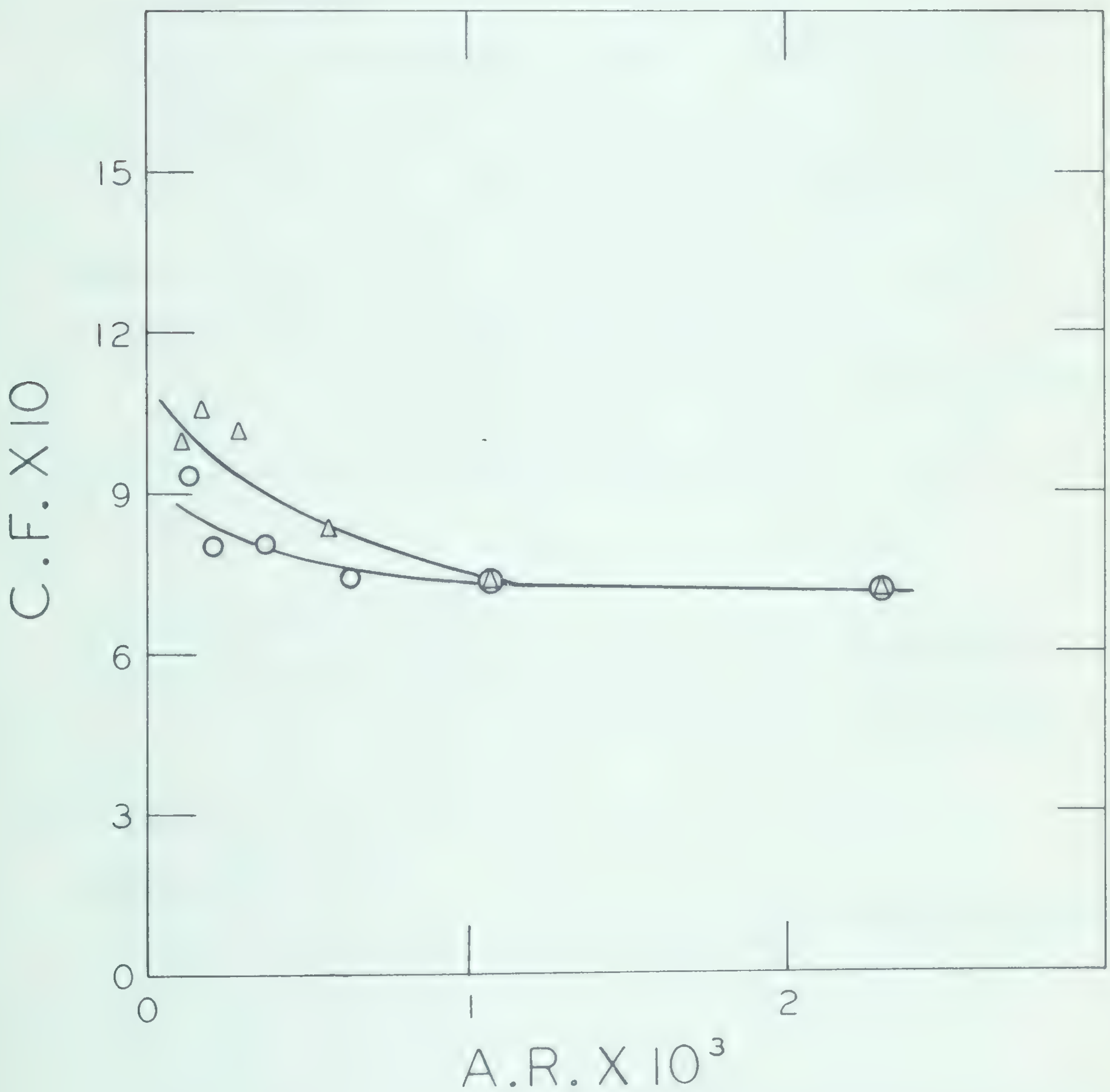
FIGURE III.16.

Dimer Calibrations

A.R. = Area of the peak / Area of cyclohexanone peak.

△ 2,2' - Diketodicyclohexyl on the Silicone grease column.

○ 2,2' - Diketodicyclohexyl on the Apiezon L column.



C.F. X 10
15
12
9
6
3
0
0
1
2
A.R. X 10^3

in Figure III.15 (solid triangles and open circles). It may be seen that the average of the G values of these two samples (solid square, Fig. III.15), as obtained by analyses on the two columns, is in agreement with the average values of the previously analysed samples (solid circles, Fig. III.15).

(ii) Individual dimers.

The values for the individual dimers, obtained by analyses of the samples referred to above on the Silicone grease column, are shown in Figures III. 17 and III.18. The G values of the individual dimers for each sample add up to the G values (total dimer, Silicone grease column) given in Figure III.15. The same uncertainty is attached to the absolute values of these yields as is attached to the value of G (total dimer) as determined from the Silicone grease column. Calibrations given in Figure III.16 were used.

2,2'-diketodicyclohexyl.

The variation with dose of the G value of 2,2'-diketodicyclohexyl is shown in Figure III. 17.A. and the G_i appears to be 0.78. The G value decreases with increasing dose.

Unknown dimer, D-1.

The value of this unknown dimer decreases with dose (Fig. III. 17.B.) and the G_i appears to be 0.42.

Unknown dimer, D-2

The value of this unknown dimer decreases with dose and is shown in Fig. III. 18.C. The G_i appears to be 0.27.

Unknown dimer, D-3.

The value of this unknown dimer seems to be constant with dose (Fig. III. 18.B.) and its G value in the dose region. 1.1 to 3.4 (10^{20} ev /ml) seems to be 0.07.

FIGURE III.17.

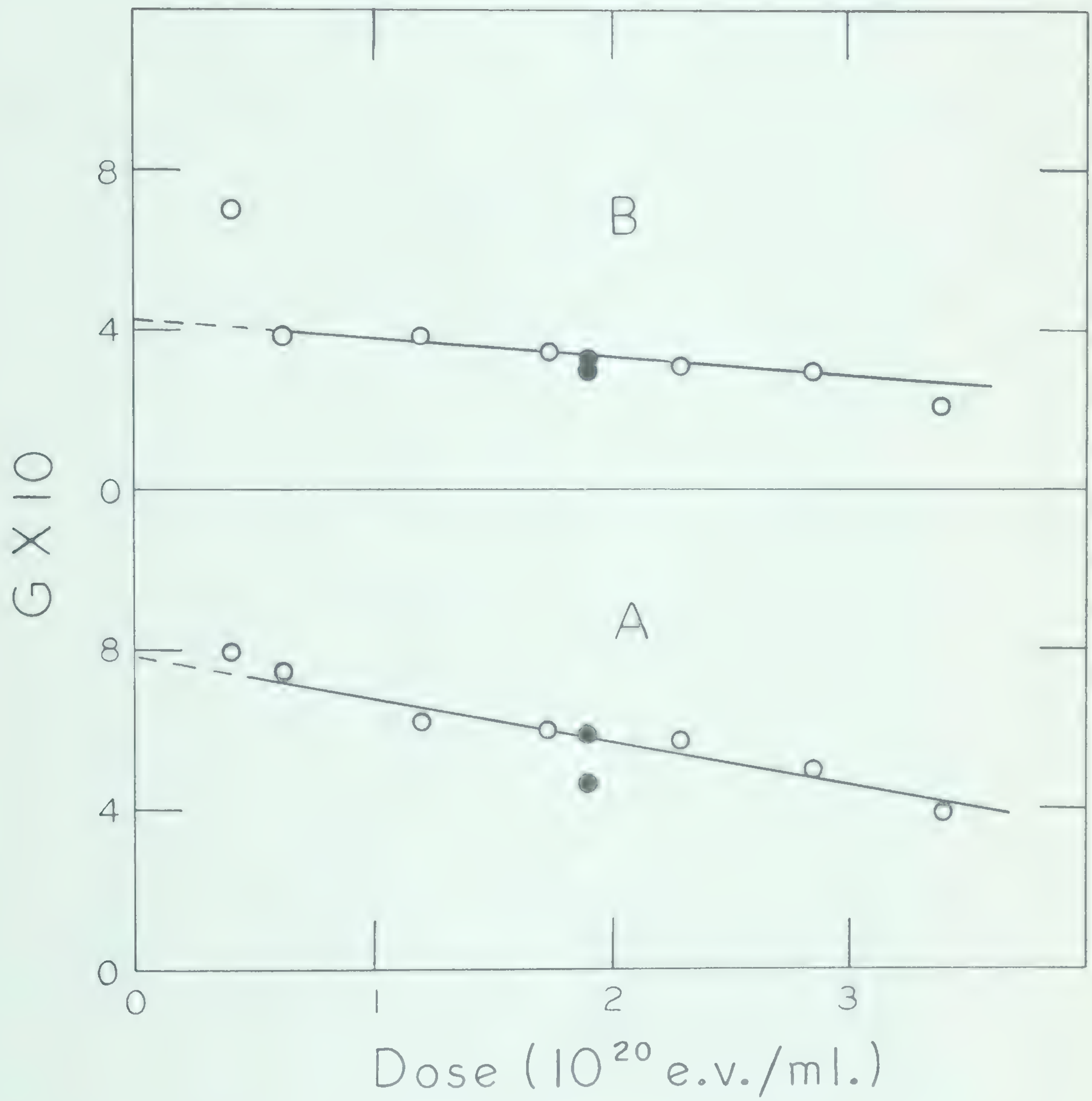
Yields of some C_{12} Products.

○ Samples analysed in Jan.'62.

● Samples analysed in Mar.'63.

A: 2,2'-Diketodicyclohexyl.

B: Unknown dimer, D-1.



B
A
8
4
0
8
4
0
G X 10
0
1
2
3
Dose (10²⁰ e.v./ml.)

FIGURE III.18.

Yields of some C_{12} Products.

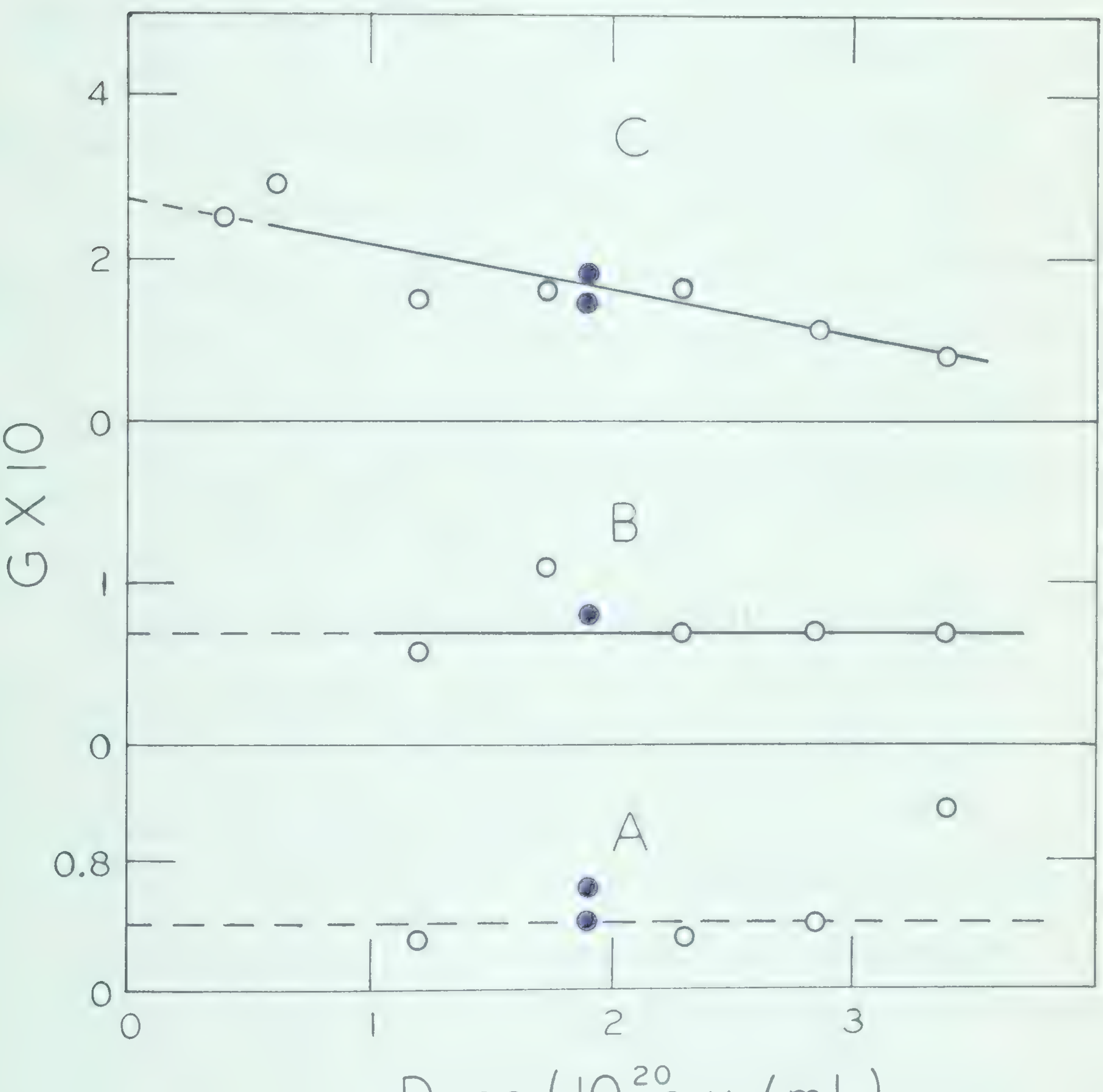
○ Samples done in Jan. '62.

● Samples done in Mar. '63.

A: Unknown dimer, D-4.

B: Unknown dimer, D-3.

C: Unknown dimer, D-2.



C
B
A
G X 10
4
2
0
1
0
0.8
0
0
1
2
3
Dose (10^{20} e.v./ml.)

Unknown dimer, D-4.

The yield of this unknown dimer is probably constant with dose (Fig. III.18.A) with the G value as 0.04 in the dose region 1.1 to 3.4 (10^{20}e v/ml).

d. Polymer.

(i). Chloroform soluble polymer.

The yield of the chloroform soluble polymer, in units of cyclohexanone molecules consumed to form polymer, is shown as a function of dose in Figure III. 19. The chloroform solutions were analysed for their cyclohexanone and dimer content on the Apiezon L column (all samples) and on the Silicone grease column (two samples). The calibrations for cyclohexanone and the dimer, in chloroform solution, are shown in Figure III.20. The polymer yield probably increases with dose and the G_i (polymer) appears to be 1.8.

One sample of cyclohexanone was irradiated ($\backsim 5 \times 10^{20}$ ev /ml) in a specially designed cell (see section II.C.4.c) and after removal of its volatile contents (in a manner exactly similar to that used for the above mentioned samples) it was sealed under vacuum and sent for microanalysis [Pascher, 1962]. The result of the microanalysis is given in Table III.7. The average composition for the samples referred to in Figure III.19 was determined (polymer: dimer: monomer ::70:19:11) and it was assumed that the sample sent for analysis had the same composition. The values required for cyclohexanone are given, for comparison.

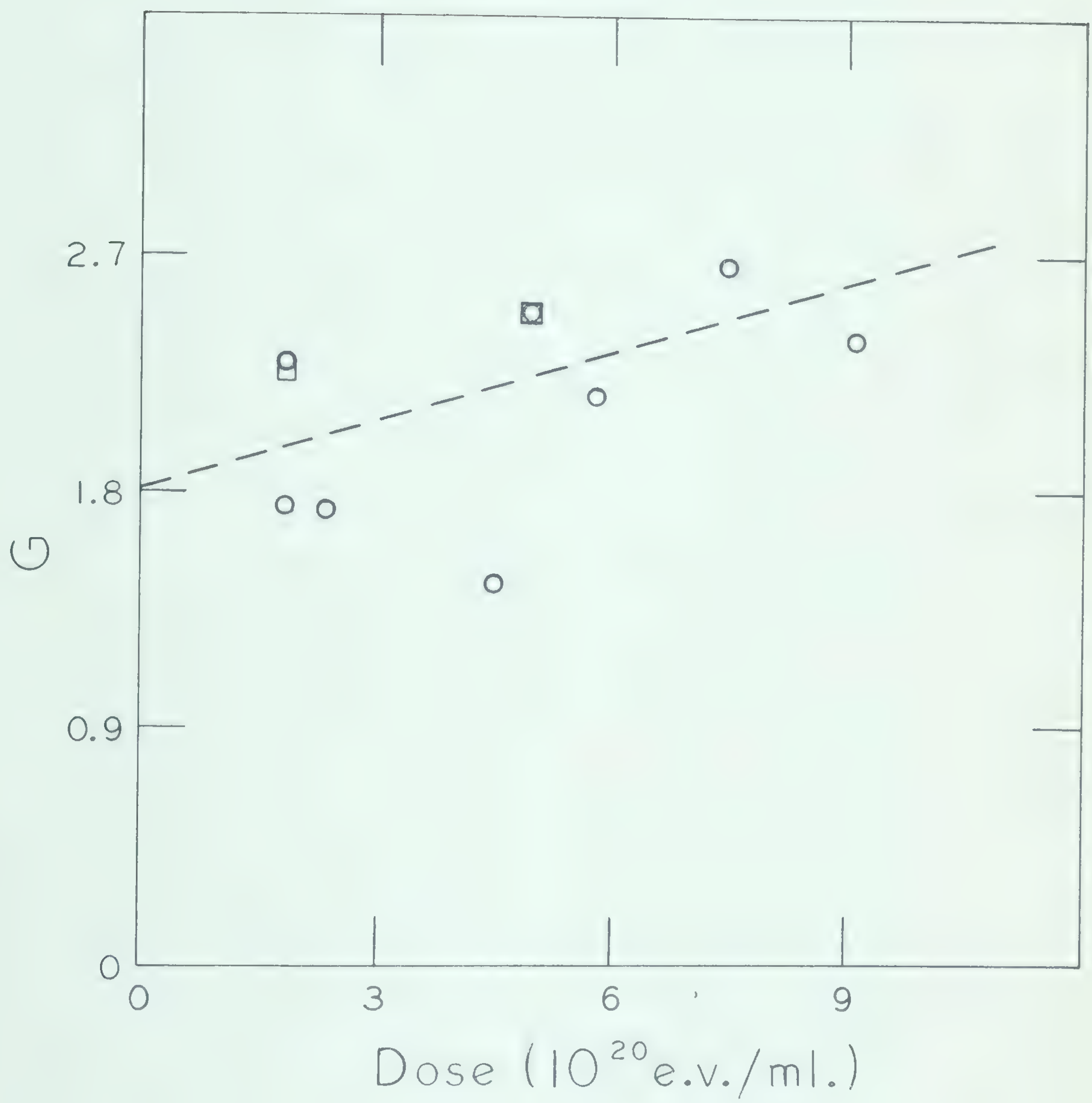
It may be seen that the C,H and O values of the polymeric mixture are broadly similar to the values required for cyclohexanone, with a slight increase in the carbon content at the cost of the hydrogen content. The molecular weight of the polymer (330) lies in between

FIGURE III.19.

Yield of Polymer.

○ Apiezon L column.

□ Silicone grease column.



2.7
1.8
0.9
0
G
0
3
6
9
Dose (10^{20} e.v./ml.)

FIGURE III.20.

Calibrations for Polymer Estimation.

A.R. = Area of the peak/ Area of cyclohexanone peak.

C.F. = Calibration factor.

A: 2,2'-Diketodicyclohexyl in chloroform solutions.

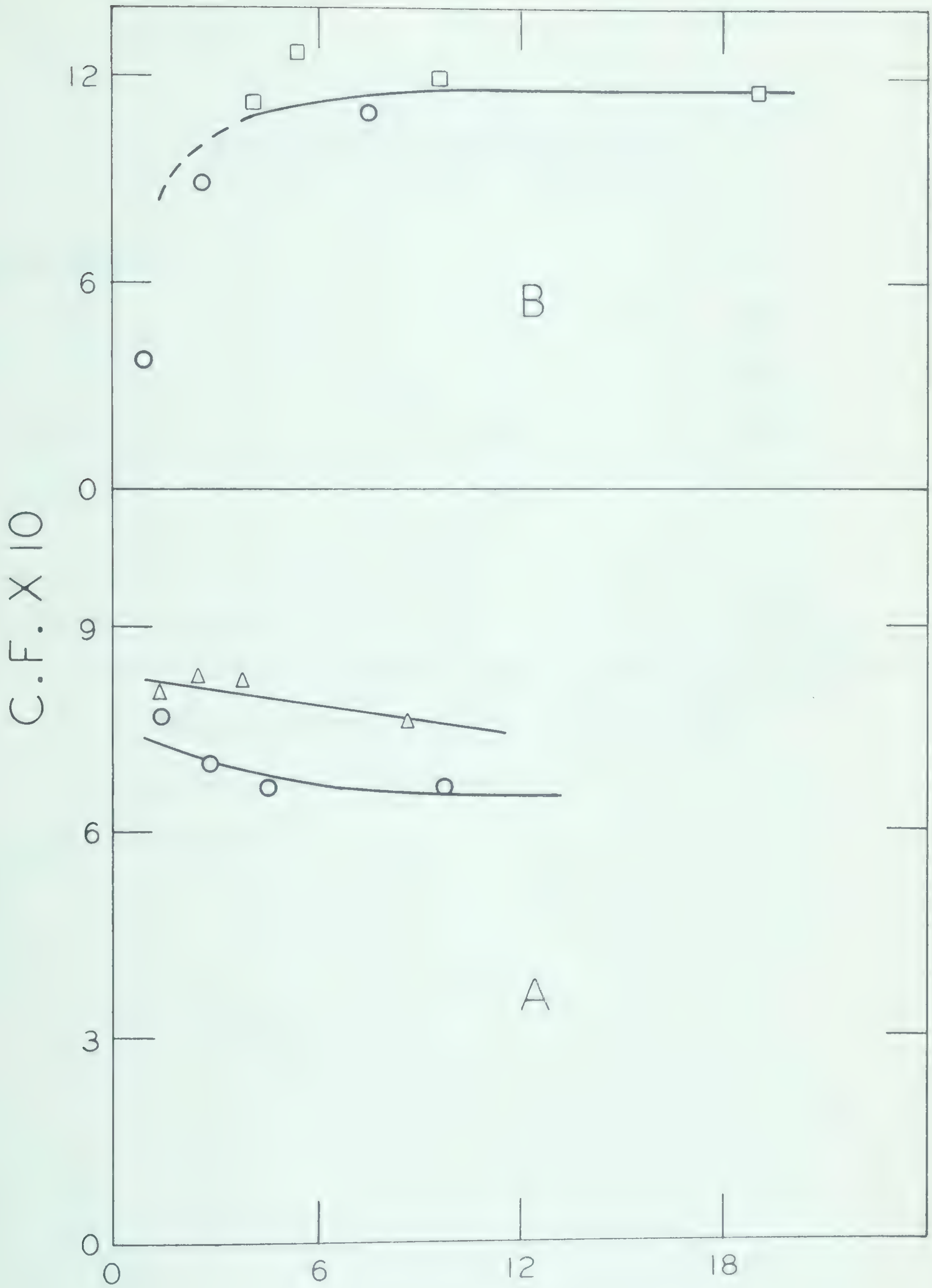
○ Apiezon L column

△ Silicone grease column

B: Cyclohexanone in Chloroform solutions.

○ Set 1; July 1962

□ Set 2; August 1963.



12
6
0
9
6
3
0
B
A
C.F. X 10
0
6
12
18
A.R. X10⁴

TABLE III.7

Microanalysis of Polymeric Mixture.

Determination	1	2
C (%)	74.1	73.4
H (%)	9.5	10.3
O (%)[a]	16.4	16.3
Mol. wt.	330	98

1: Results for the polymeric mixture (mentioned in d.i above). All values are averages of two determinations.

2: Values required for cyclohexanone.

a. By difference.

that required for the trimer (290) and tetramer (386) of cyclohexanone.

(ii). Chloroform insoluble polymer.

Some of the glass bulbs, which were used for irradiating cyclohexanone for work referred to in (i) above, were analysed for insoluble polymer [Pascher, 1962]. On the basis of analyses of bulbs from four samples (and two blanks), the average G (insoluble polymer) was calculated to be about 0.1.

B. Cyclohexanone Solutions.

Various solutions of benzene and of 2,3-dimethyl-1,3-butadiene in cyclohexanone were irradiated to a constant absorbed dose [5.92 $\pm$ 0.12 (10^{-4} ev /e^-), which is about 1.9 x 10^{20} ev/ml] and the yields of various products were measured as a function of the electron fraction (ϵ_s) of the solute.

$$\epsilon_s = \frac{\text{moles of electrons of the solute in the solution.}}{\text{total moles of electrons in the solution.}} \quad \text{--- (III.1)}$$

Two samples of cyclohexanone with added oxygen were also irradiated and analysed to briefly compare the effect of oxygen with that of 2,3-dimethyl-1,3-butadiene on the formation of the major liquid products of radiolysis of cyclohexanone.

1. Fragmentation products.

a. -196° and -150° fractions.

The G values of these two gaseous fractions from the irradiated solutions of 2,3-dimethyl-1, 3-butadiene and of benzene in cyclohexanone are shown in Figure III.21.

The G values for the -196° fraction decrease gradually with increasing concentration of the solute, the decrease being more pronounced for the 2,3-dimethyl-1,3-butadiene solutions in the low concentration region ($\epsilon_s < 0.1$, Fig. III.21.A).

FIGURE III.21

Gaseous Products from Solutions.

ϵ_s = Electron fraction of the solute.

Dose = 5.92 ± 0.12 (10^{-4} ev./e^-).

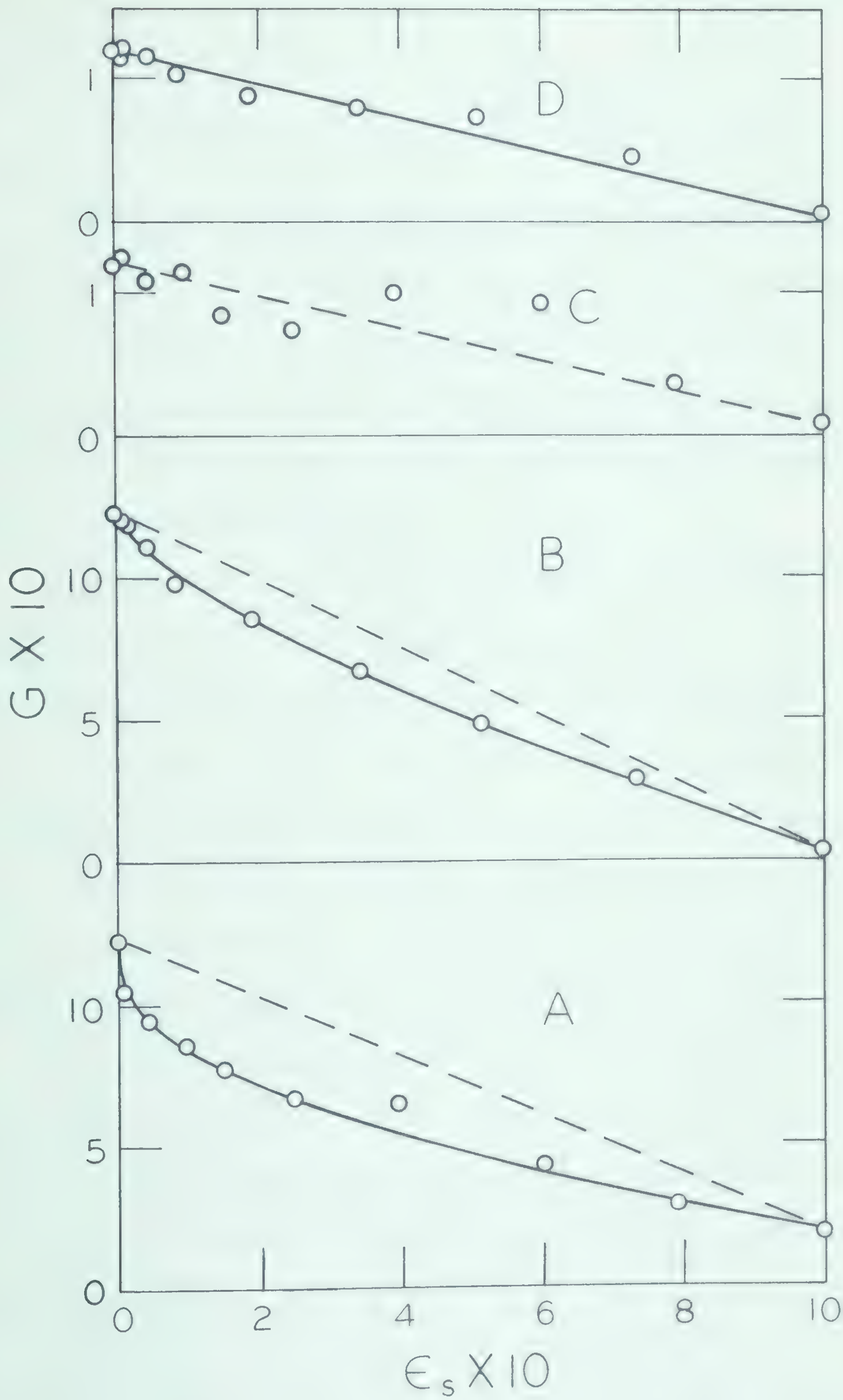
Dashed lines refer to G_{ex}

A: -196° fraction; 2,3-dimethyl-1,3-butadiene solutions.

B: -196° fraction; benzene solutions.

C: -150° fraction; 2,3-dimethyl-1,3-butadiene solutions.

D: -150° fraction; benzene solutions.



D
C
B
A
0
1
0
1
0
5
10
0
5
10
0
2
4
6
8
10
G X 10
ϵ_s X 10

If the radiolysis of a component X in a binary solution is unaffected by the presence of the other component Y, then the expected G value (G_{ex}) for a product P from the solution should be given by the expression III.2.

$$G_{ex}(P) = G^{o}_{x}(P)\,\epsilon_{x} + G^{o}_{y}(P)\,\epsilon_{y} \quad \text{----------------------} \quad (III.2)$$

where $G^{o}_{x}(P)$ and $G^{o}_{y}(P)$ refer to the G values of the product P from pure X and pure Y respectively, and ϵ_x and ϵ_y refer to the electron fraction of the components X and Y respectively, in the solution radiolysed. The values of G_{ex} in these Figures are represented by linear dashed lines. Most of the end points are averages of more than one determination.

Hydrogen and carbon monoxide were the only observable constituents of the - 196° fraction from the solutions of 2,3-dimethyl-1,3-butadiene and of benzene in cyclohexanone.

The G values for the -150° fraction from the benzene solutions decrease linearly with increasing electron fraction of benzene (Fig. III.21.D) and the decrease in the G values for this fraction from the 2,3-dimethyl-1,3-butadiene solutions also seems to be roughly linear with increasing electron fraction of the solute (Fig. III.21.C).

Ethylene was found to be the main constituent of the -150° fraction, though traces of ethane, acetylene and propane could be seen in some samples. Propylene was also a constituent of this fraction but it did not seem to be getting separated quantitatively from the liquid, at this temperature.

b. Hydrogen.

The variation of the yield of hydrogen with the concentration of the solute is shown in Figures III.22.A and III.22.B. for the

FIGURE III.22

Hydrogen and Carbon Monoxide

ϵ_s = Electron fraction of solute.

Dose = 5.92 ± 0.12 (10^{-4} ev /e^-)

Dashed lines refer to G_{ex}

A: 2,3-Dimethyl-1, 3-butadiene solutions.

○ H_2 △ C_2H_4*

● G_i (H_2) ▲ G_i (C_2H_4)*

B: Benzene solutions.

○ H_2 △ C_2H_4*

● G_i (H_2) ▲ G_i (C_2H_4)*

C: 2,3-Dimethyl-1, 3-butadiene solutions.

CO

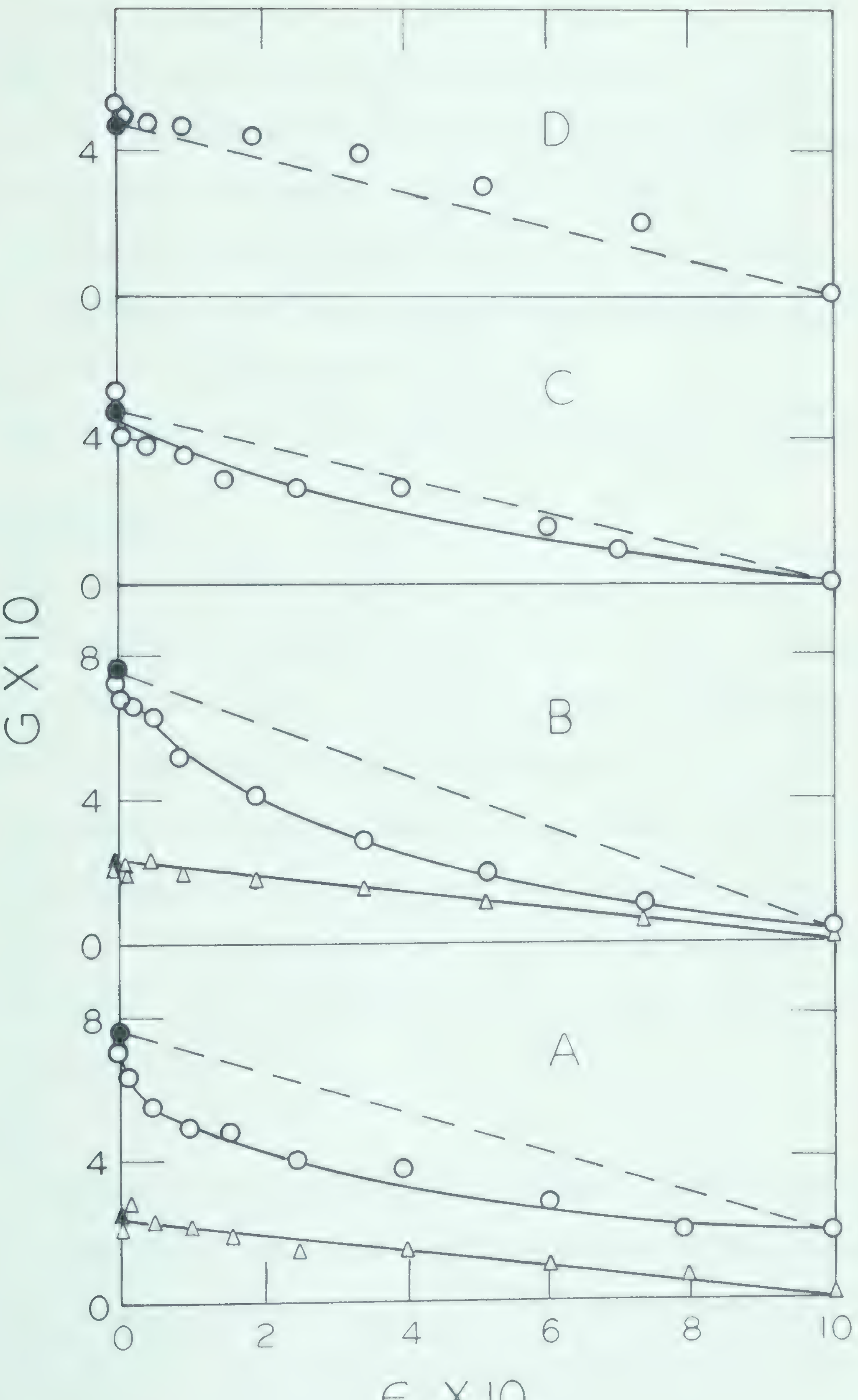
● G_i (CO)

D: Benzene solutions.

○ CO

● G_i (CO)

* The values for ethylene are given as GX20



D
C
B
A
G X 10
0
4
0
4
0
4
8
0
4
8
0
2
4
6
8
10
ε_s X 10

benzene and the 2,3-dimethyl-1,3-butadiene solutions respectively. In both cases the G value decreases gradually with the increasing concentration of the solute, the decrease being more pronounced for the diene solutions in the low concentration region ($\epsilon_s < 0.1$). However, the decrease is seen to be greater than would be expected on the basis of the expression III.2 in both the cases.

The $G(H_2)$ for pure benzene is found to be 0.038 (compare $G(H_2) = 0.038$ at 2×10^{20} ev./ml [Van Dusen and Hamill, 1962] and $G(H_2) = 0.19$ for 2,3-dimethyl-1,3-butadiene.

The calibration for hydrogen is shown, in Figure III.23.

c. Carbon monoxide.

The yield of carbon monoxide as a function of the electron fraction of solutes is shown in Figure III.22, C and D. For the 2,3-dimethyl-1, 3-butadiene solutions the G (CO) obtained seems to decrease gradually with increasing concentration of the diene, all the values obtained being lower than the G_{ex} values. For the benzene solutions, though the G (CO) decreases with increasing benzene concentration, the G values obtained seem to be greater than G_{ex} (Fig. III.22.D). The calibration for carbon monoxide is shown in Figure III.24.

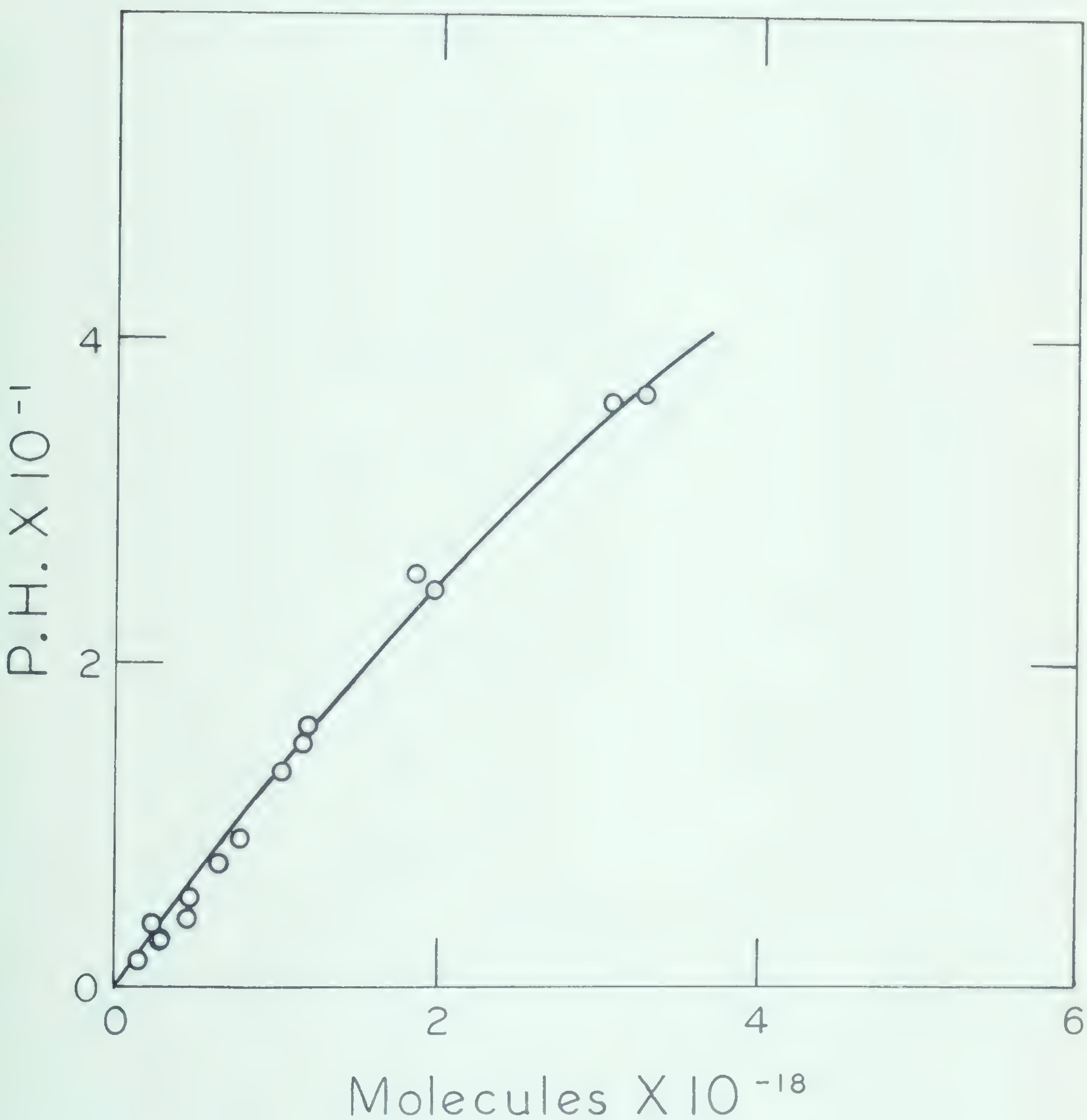
d. Ethylene.

The yield of ethylene is shown in Figures III.22 A and B, for the 2,3-dimethyl-1,3-butadiene and the benzene solutions, respectively. It seems to decrease linearly with the increasing electron fraction of the solute, in both cases. The calibration for ethylene is shown in Figure III.25.

FIGURE III. 23

Hydrogen Calibration.

P.H. = Peak height; [Unit, 1/32"].

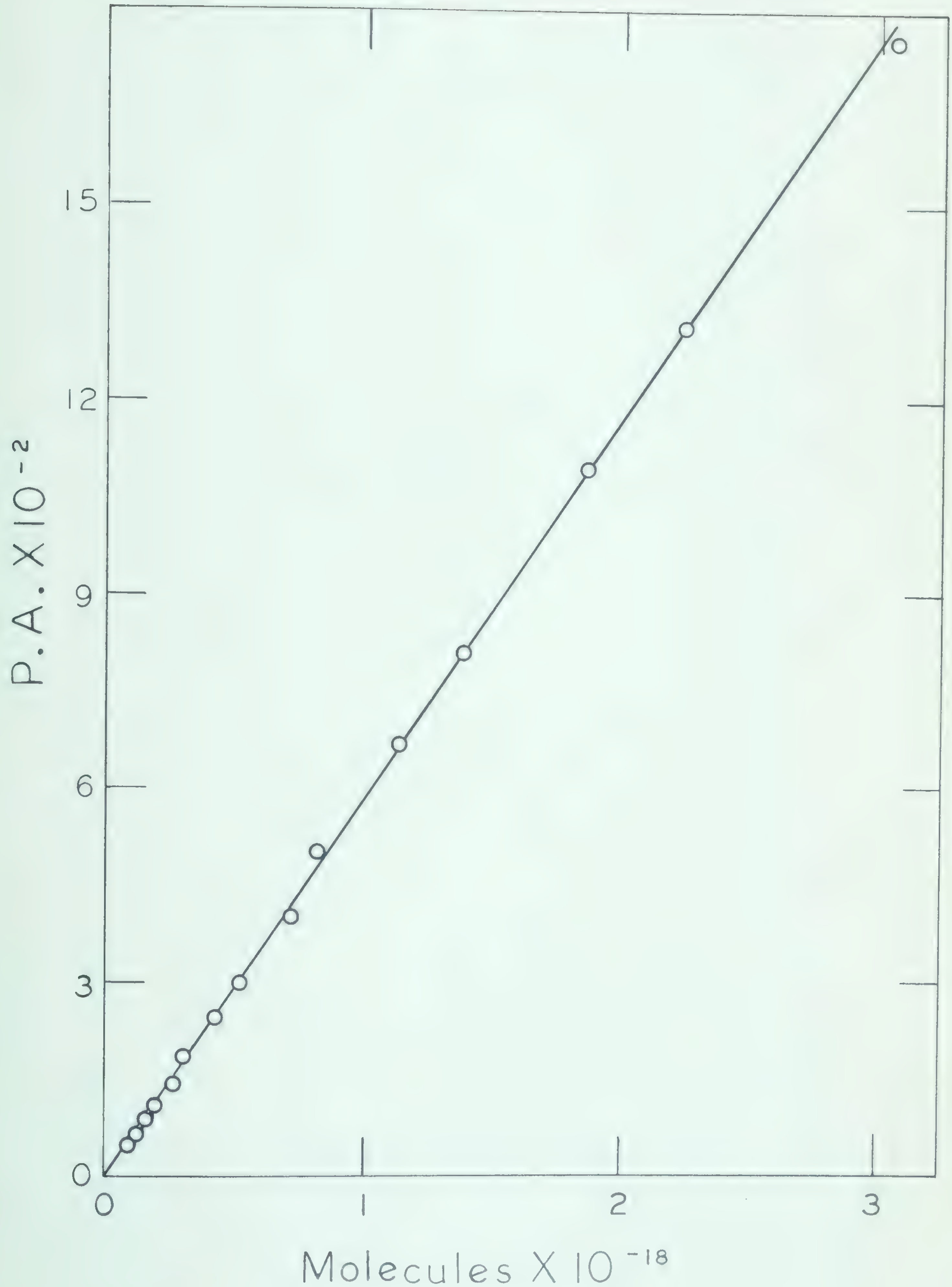


P.H. X 10^-1
0
2
4
0
2
4
6
Molecules X 10^-18

FIGURE III.24.

Carbon Monoxide Calibration.

P.A. = Peak area; [Unit, $(1/32")^2$]

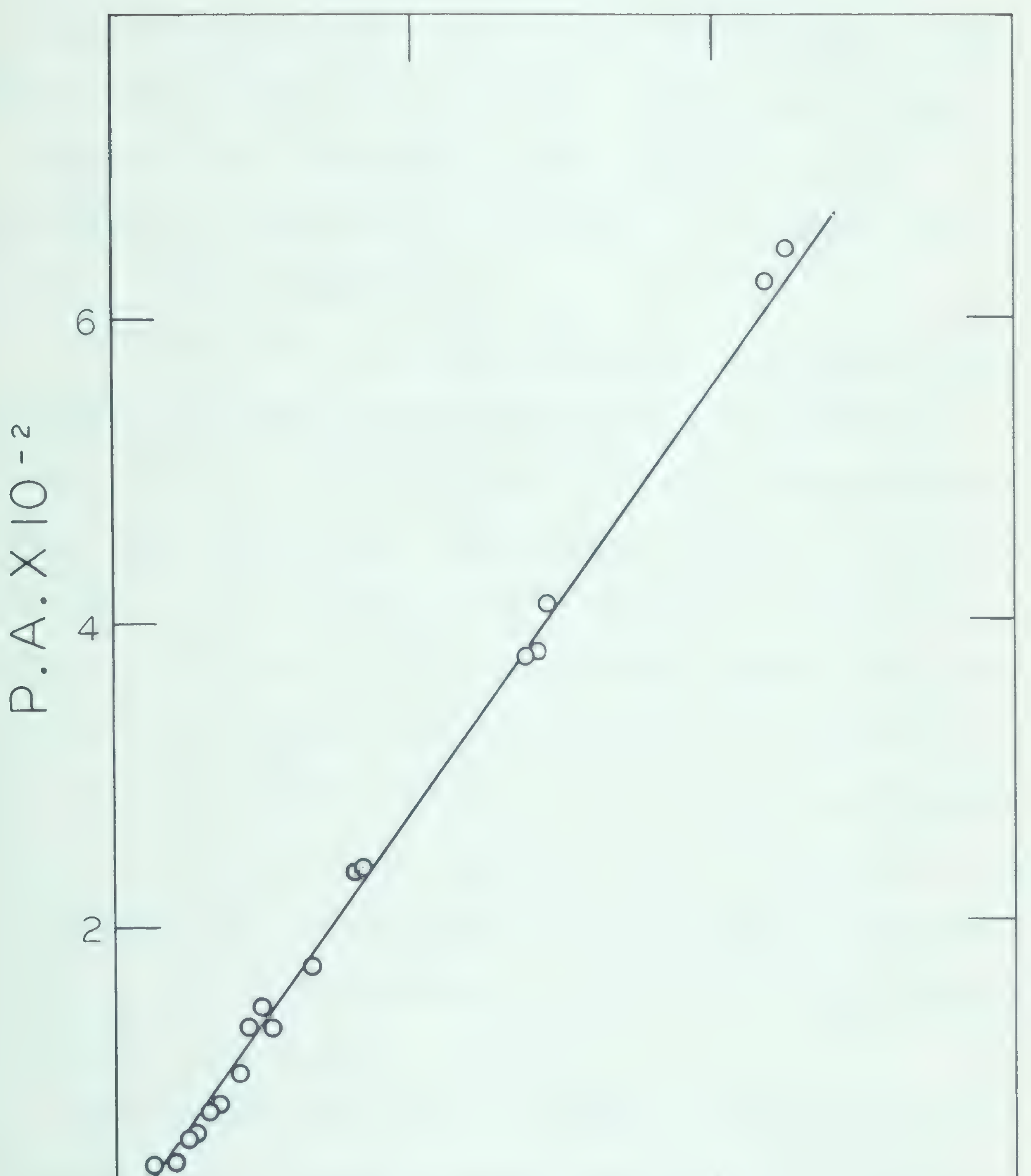


15
12
9
6
3
0
P.A. X 10⁻²
0
1
2
3
Molecules X 10⁻¹⁸

FIGURE III.25

Ethylene Calibration

P.A. = Peak area; [Unit, $(1/32")^2$].


P.A. X 10 -2
0
2
4
6
0
6
12
18
Molecules X 10 -17

e. <u>1-Pentene, n-pentane and 2-pentene.</u>

The combined yield of these three hydrocarbons could be measured for the benzene solutions only, by analyses of the irradiated solutions on the Ucon and the Silicone grease columns. The combined yield is shown in Figure III.26.A, and it seems to increase at first followed by a gradual decrease, with the increasing concentration of benzene, most of the values being greater than G_{ex} (dashed line).

The calibration on the Silicone grease column was done using solutions containing 1-pentene and n-pentane and is shown in Figure III.27.B. The calibrations on the Ucon column were done using 1-pentene solutions, and are shown in Figures III.27.A and III.28. In the radiolysis of pure cyclohexanone 1-pentene is the major C_5 product (G = 0.22), n-pentane and 2-pentene being minor products (G = 0.023 and 0.004 respectively). So the error due to the use of 1-pentene calibration for all the three C_5 open chain hydrocarbon products, for their estimation on the Ucon column, is likely to be negligible.(So also, the error due to absence of 2-pentene in the calibration solutions used on the Silicone grease column is likely to be negligible).

These products could not be measured in the 2,3-dimethyl-1, 3-butadiene solutions due to interference by the solute in the analyses.

The C_5 products were also measured (Ucon column) in the oxygen containing samples and the yields are given in Table III.8.

Oxygen seems to reduce the yield of these C_5 open chain hydrocarbons even at this low concentration.

FIGURE III.26.

C_5 Hydrocarbons and Cyclohexanol

ϵ_s = Electron fraction of the solute.

Dose = 5.92 ± 0.12 (10^{-4} ev/e-).

Dashed lines refer to G_{ex}

A: Benzene stolutions.

○ 1-Pentene + n-pentane + 1-pentene; Ucon column.

□ 1-Pentene + n-pentane + 1-pentene; Silicone grease column.

△ Cyclopentane*; Silicone grease column.

B: Benzene solutions.

○ Cyclohexanol; Ucon column.

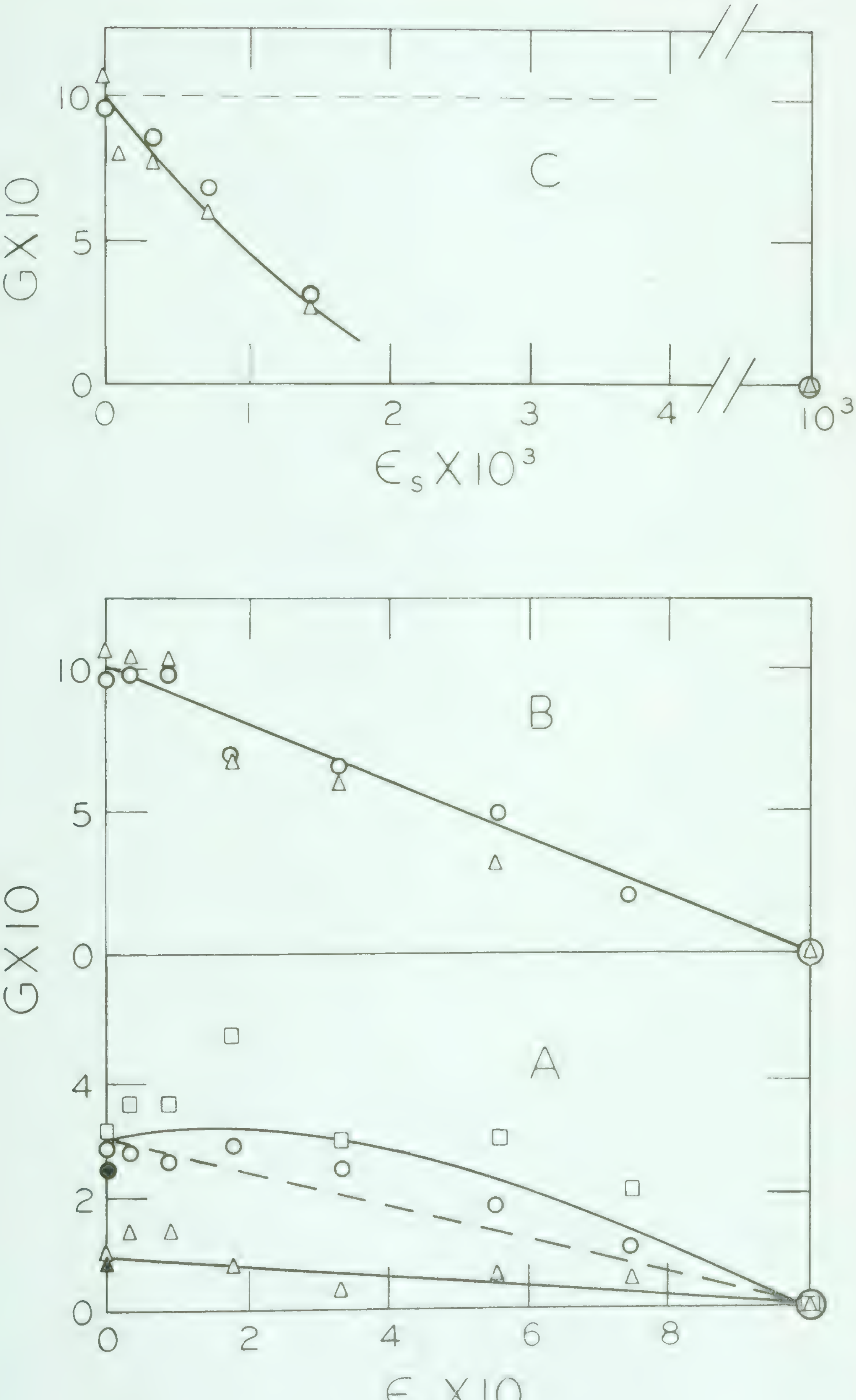
△ Cyclohexanol; Carbowax column.

C: 2,3-Dimethyl-1,3-butadiene solutions.

○ Cyclohexanol; Ucon column.

△ Cyclohexanol; Carbowax column.

* The values for cyclopentane are given as GX20



C
B
A
G X 10
G X 10
10
5
0
4
2
0
1
2
3
4
10^3
6
8
$\epsilon_s \times 10^3$
$\epsilon_s \times 10$

FIGURE III. 27

Calibrations for C_5 Hydrocarbons.

C.F. = Calibration factor.

P.R. = Peak ratio.

A: 1-Pentene; Ucon column.

○ 80 μl injections.

△ 24 μl injections.

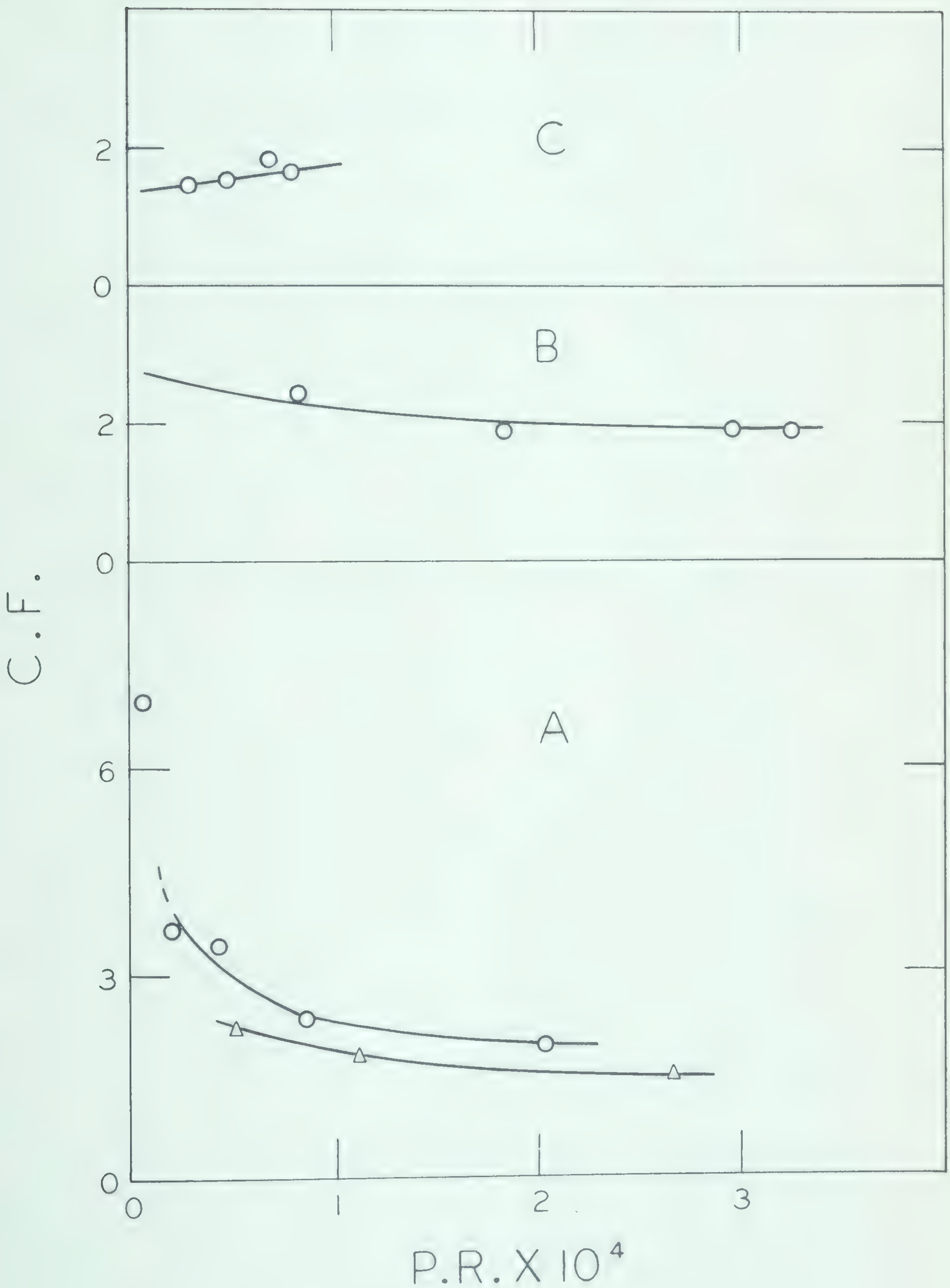
$$P.R. = \frac{\text{Height of 1-pentene peak, [Unit, 1/32"]}}{\text{Area of cyclohexanone peak [Unit, (1/32")}^2\text{]}}$$

B: 1-Pentene + n-pentane; Silicone grease column.

$$P.R. = \frac{\text{Area of 1-pentene + n-pentane peak}}{\text{Area of cyclohexanone peak}}$$

C: Cyclopentane; Silicone grease column.

P.R: The same as in B. above.



C
B
A
C.F.
P.R. X 10⁴
0
2
0
2
0
3
6
0
1
2
3

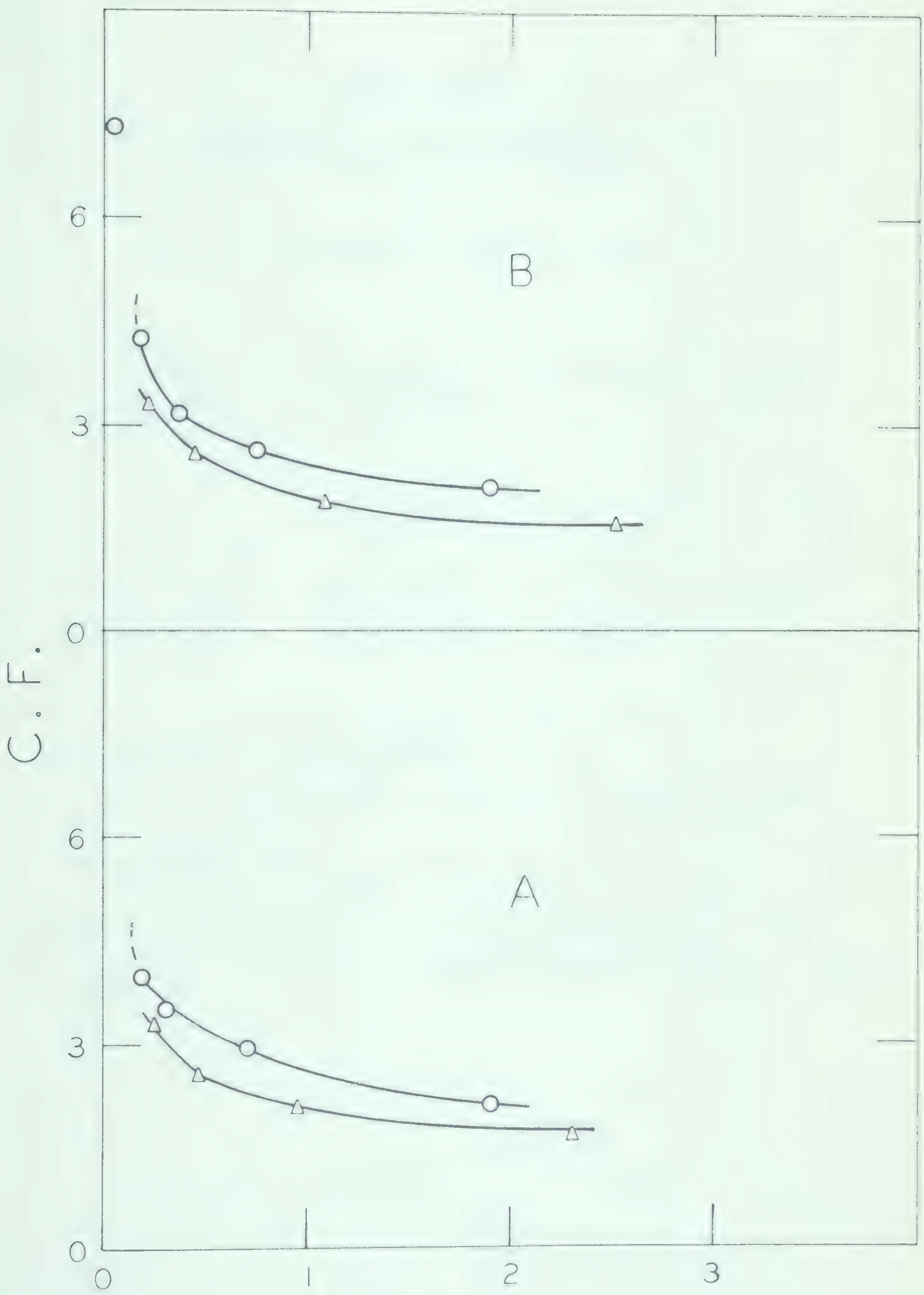
FIGURE III. 28

1-Pentene Calibrations on the Ucon Column

C.F. = Calibration factor

$$\text{P.R.} = \frac{\text{Height of 1-pentene peak, [Unit, 1/32"]}}{\text{Area of cyclohexanone peak, [Unit, }(1/32")^2\text{]}}$$

		Volume injected (μl)
A:	○	100
	△	64
B:	○	90
	△	40



B
A
C. F.
6
3
0
6
3
0
0
1
2
3
P.R. X 10

TABLE III.8

Products from Oxygen Solutions.

Dose = 5.92 ± 0.12 (10^{-4} ev /e^-).

Pressure of O_2 in the Sample[a]	Electron fraction[b] of O_2.	G(Pentene + + Pentane)	G(5-Hexenal)	G(Peroxides).
0 mm	0	0.29 ± 0.02	0.56 ± 0.03	$\leqslant$ 0.3
71 mm	$\sim 2.5 \times 10^{-5}$	0.21 ± 0.02	0.22 ± 0.02	2.5 ± 0.2
412 mm	$\sim 14.6 \times 10^{-5}$	0.20 ± 0.02	0.15 ± 0.02	3.5 ± 0.2

a. Cyclohexanone, 2 ml; Oxygen, $\sim$ 10 ml.

b. To calculate the electron fraction of dissolved oxygen, its solubility has been assumed to be 0.2 ml per ml of the ketone on the basis of the values for the solubility of oxygen in some oxygenated organic compounds [Loomis, 1928].

f. Cyclopentane.

The variation of the G value of cyclopentane with the concentration of benzene is shown in Figure III.26A and the calibration is shown in Figure III.27C. Its G value seems to decrease linearly with increasing benzene concentration. The measurements were done using the Silicone grease column.

2. C_6 products.

a. Cyclohexanol.

The yields of cyclohexanol from the benzen solutions and the 2,3-dimethyl-1,3-butadiene solutions are shown in Figure III.26 (B and C). A sharp contrast is noticeable in the two cases. The yield seems to decrease linearly with the increasing electron fraction of benzene. However, in the case of the diene solutions the G values for cyclohexanol fall very rapidly, so much so that cyclohexanol was not visible as a product in the samples containing greater than about 2×10^{-3} electron fraction of the diene.

The calibrations for cyclohexanol are shown in Figures III.29 (Carbowax column) and III.30 (Ucon column). The cyclohexanol yield could not be determined in the oxygen solutions due to uncertainty in the blank value.

b. 5-Hexenal.

The yields of 5-hexenal from the benzene solutions and from the 2,3-dimethyl-1,3-butadiene solutions are shown in Figure III.31 and a marked difference is evident in the two cases. For the benzene solutions, the yield of 5-hexenal increases with increasing benzene concentration, decreasing gradually after about $\epsilon_s \sim 0.5$. The sample with $\epsilon_s = 0.333$ on analysis gave the 5-hexenal peak almost at the end

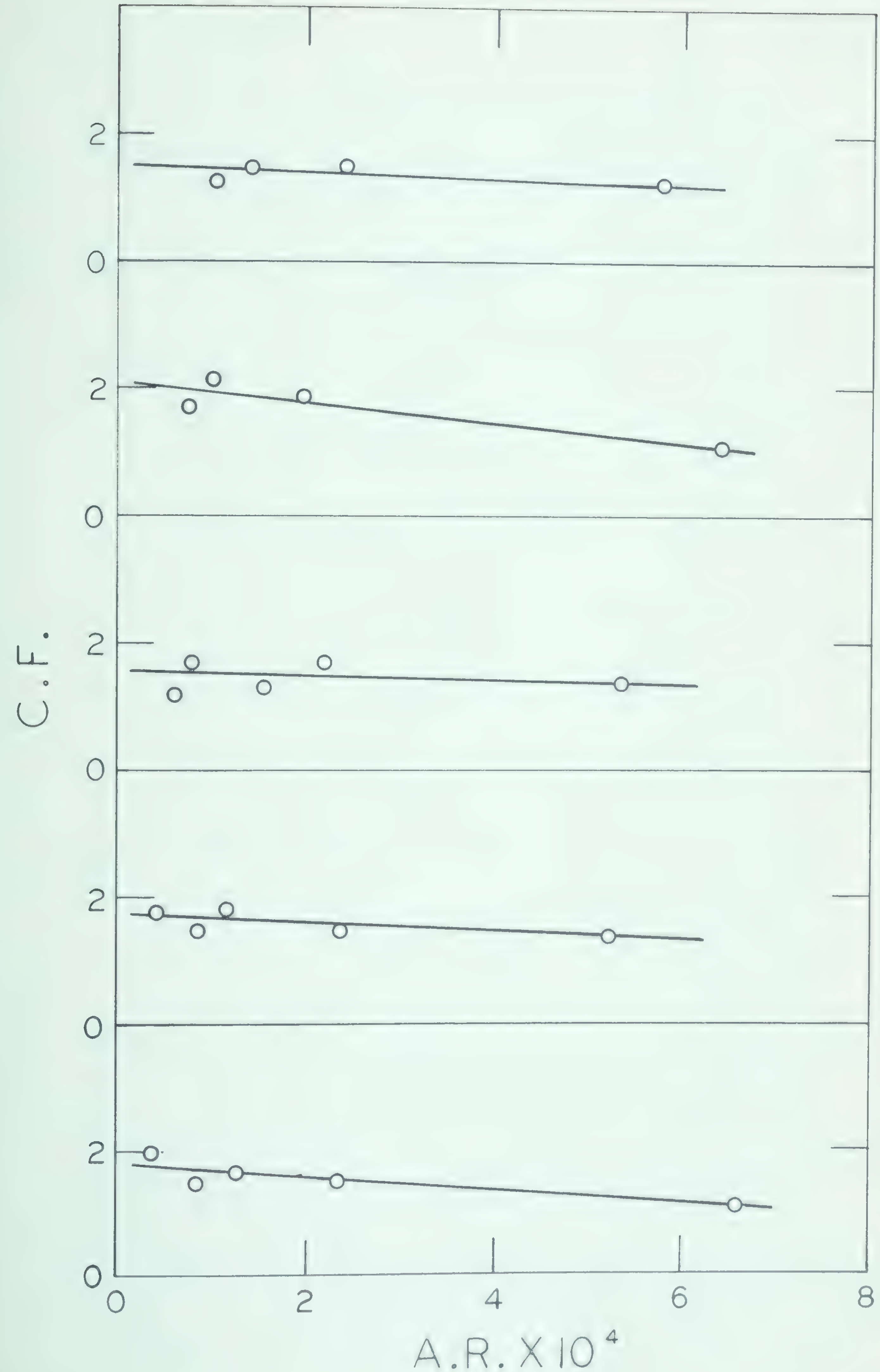
FIGURE III. 29.

Cyclohexanol Calibrations on the Carbowax Column.

A.R. = Area of the peak/ Area of cyclohexanone peak.

C.F. = Calibration factor.

	Volume injected (μl)
A.	100
B.	90
C.	80
D.	64
E.	40



C.F.
0
2
0
2
0
2
0
2
0
2
0
2
4
6
8
A.R. X 10⁴

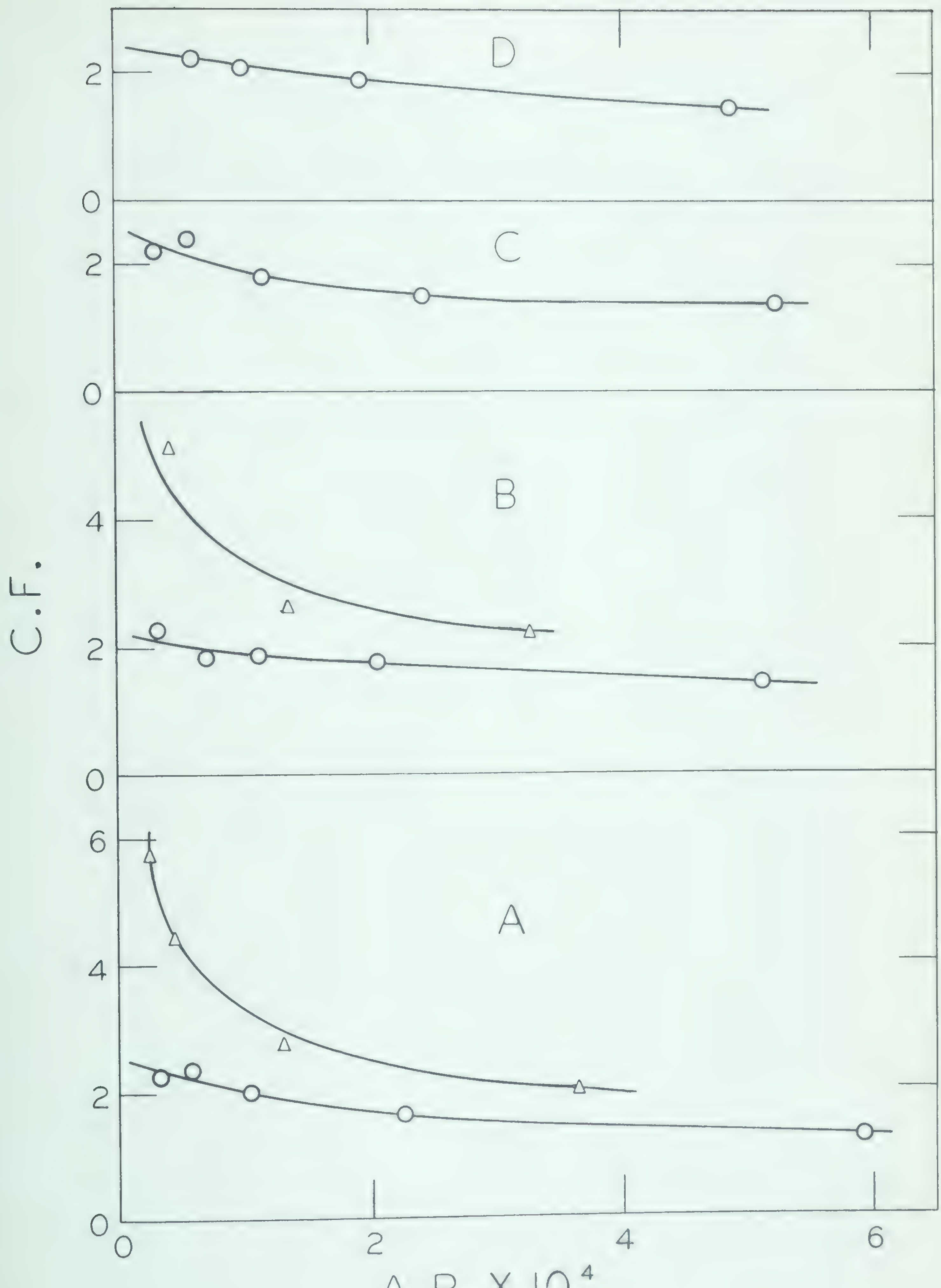
FIGURE III. 30.

Cyclohexanol Calibrations on the Ucon Column.

A.R. = Area of the peak/ Area of cyclohexanone peak.

C.F. = Calibration factor.

		Volume injected (μl)
A.	○	100
	△	40
B.		90
	△	24
C.		80
D.		64.



D
C
B
A
C.F.
A.R. X 10⁴
0
2
4
6

FIGURE III. 31.

5-Hexenal Yields from the Solutions

ϵ_s = Electron fraction of the solute.

Dose = 5.92 ± 0.12 (10^{-4} ev /e^-)

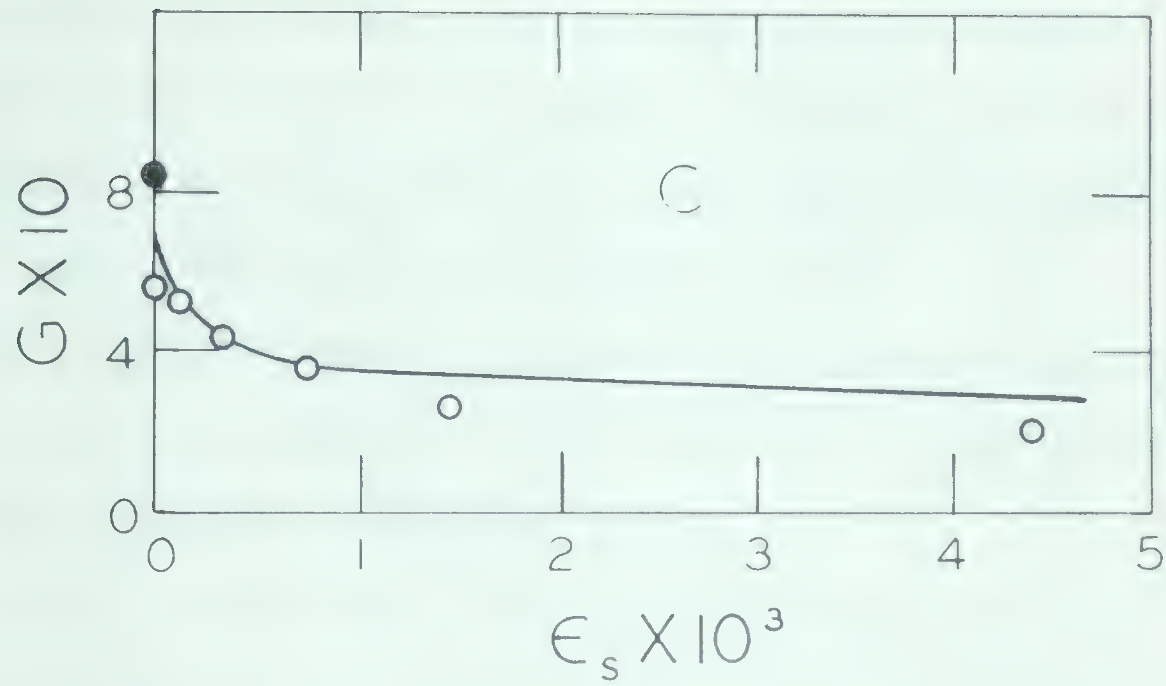
A: Benzene solutions.

○ 5-Hexenal; calculated on the basis of calibration factors in terms of cyclohexanone. No overlap with benzene.

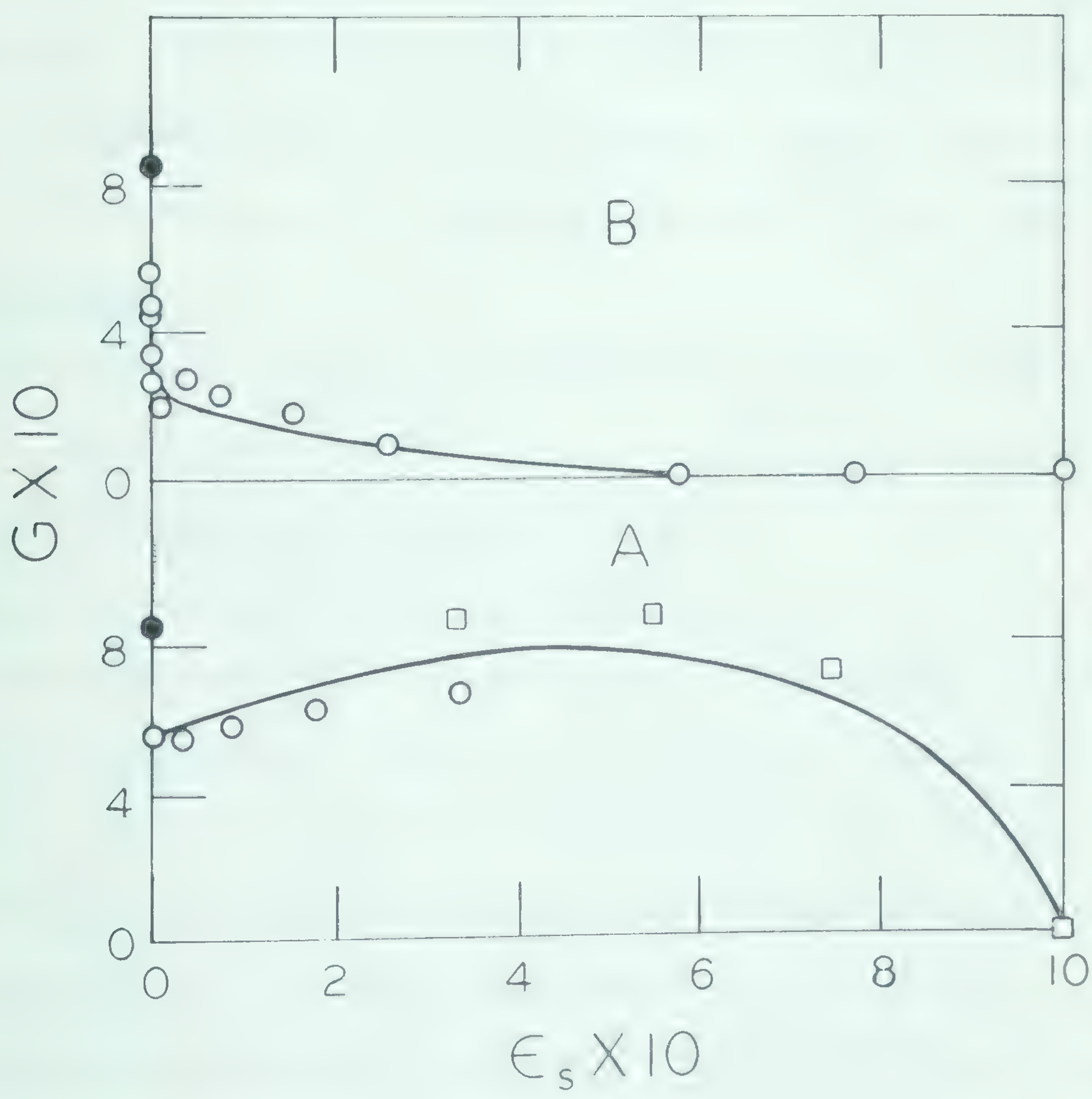
□ 5-Hexenal; calculated on the basis of calibration factors in terms of benzene. Overlap with benzene.

B: 2,3-Dimethyl-1,3-butadiene solutions.

C: " " " "



C
G X 10
8
4
0
0
1
2
3
4
5
ϵ_s X 10^3



B
A
G X 10
8
4
0
8
4
0
0
2
4
6
8
10
ϵ_s X 10

of the tail of the benzene peak. Therefore, for this sample the G value for 5-hexenal was calculated firstly by assuming no overlap with the benzene peak(tail) and using the calibration factor in terms of cyclohexanone (Fig. III.32) and secondly by assuming overlap and using the calibration factor in terms of benzene (Figs. III.33 and III.34). Both of these values are given in Figure III.31.A.

For the 2,3-dimethyl-1, 3-butadiene solutions, the G value of 5-hexenal drops very rapidly at first (Fig. III.31, B and C) and then decreases more slowly (beyond $\epsilon_s \sim 0.02$).

Oxygen also decreased the yield of 5-hexenal and the G values are given in Table III.8. Oxygen seems to reduce the yield of 5-hexenal to a greater extent than does 2,3-dimethyl-1, 3-butadiene. It may be mentioned that a small broad peak was observed in the same region, right under the 5-hexenal peak, in both the samples. However, the same broad peak was also visible in the unirradiated oxygen solution (blank).

c. Cyclohexenone.

The radiolytic yield of cyclohexenone, from pure cyclohexanone, is small (G= 0.2, Fig III.12) at $\sim 1.9 \times 10^{20}$ ev /ml. It could not be seen as a product in any of these solutions.

d. Additional products from oxygen solutions.

The main product peak after the cyclohexanone peak, obtained by analysis of the irradiated solutions on the Apiezon L column, was tentatively identified as a hydroxycyclohexanone or a cyclohexanedione by comparison of its retention time with that of quinone and hydroquinone. The G values for this product were estimated to be $\sim$0.8 and $\sim$1.2 from the samples with pressure of oxygen equal to 71 mm and 412 mm respectively, assuming the calibration factor to be $\sim$1. One of the three minor products

FIGURE III.32.

5-Hexen-2-one and 2,3-Dimethyl-1,3-butadiene calibrations

A.R. = Area of the peak/ Area of the cyclohexanone peak.

C.F. = Calibration factor.

□ 5-Hexen-2-one; Ucon column (x = 4)

△ 2,3-Dimethyl-1,3-butadiene; Silicone grease column (x =3).

○ 2,3-Dimethyl-1,3-butadiene; Apiezon L column (x = 3)

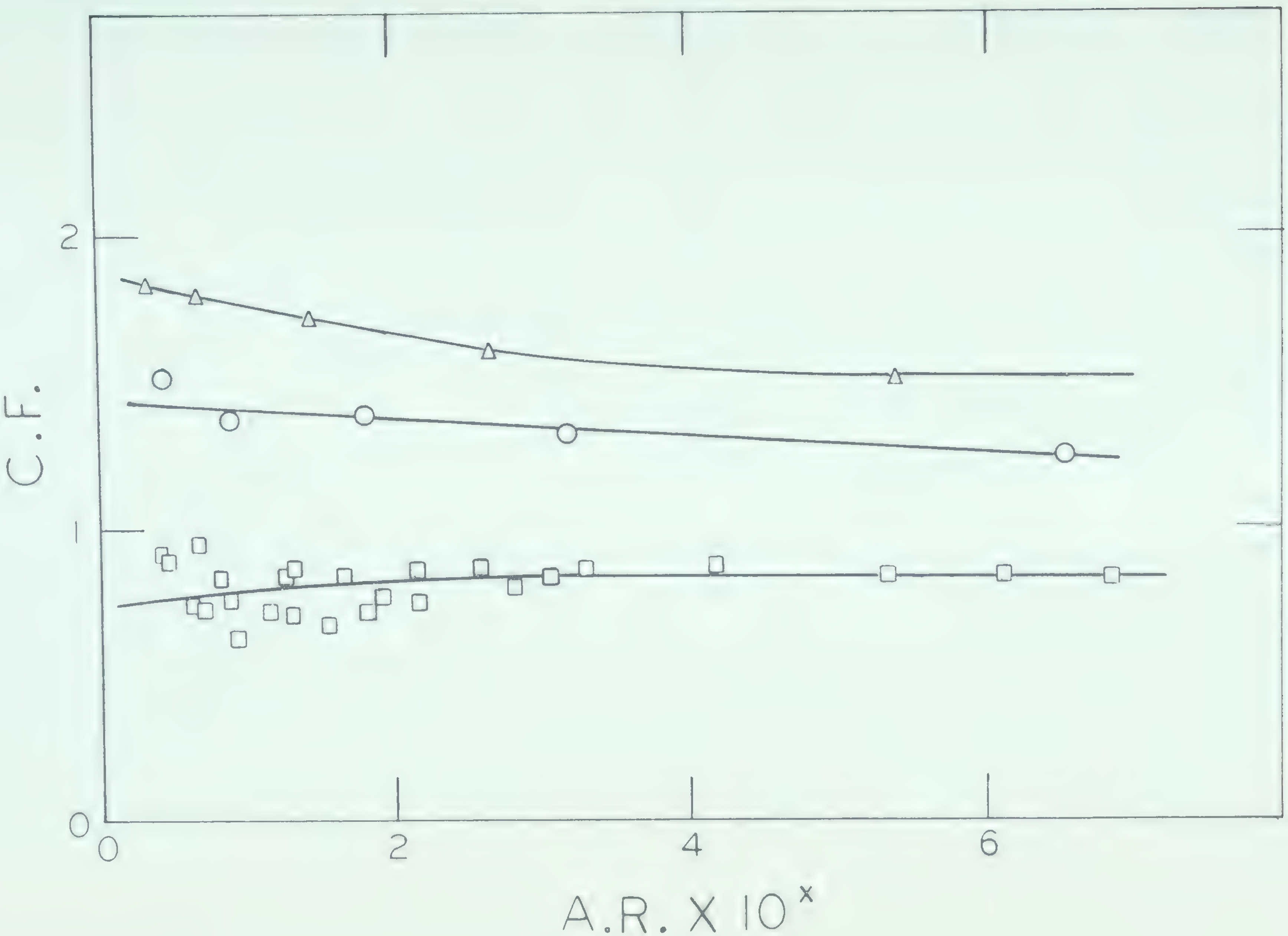

C.F.
2
1
0
0
2
4
6
A.R. X 10^x

FIGURE III. 33

Calibrations of 5-Hexen-2-one in Benzene Solutions on the Ucon Column.

A.R. = Area of the peak/ Area of cyclohexanone peak.

C.F. = Calibration factor.

	Volume injected (μl)
A.	100
B.	76
C.	58

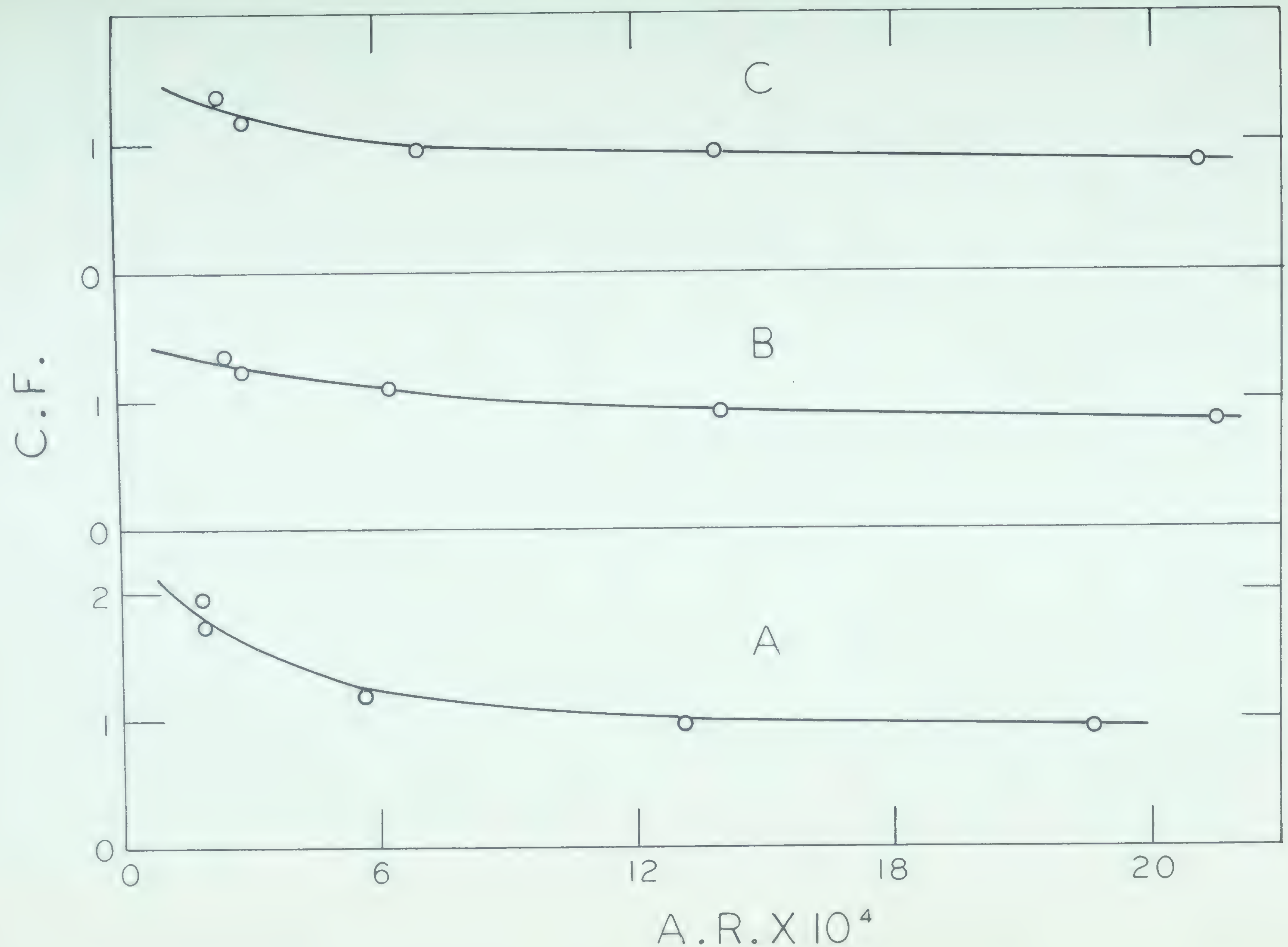

C
B
A
C.F.
1
0
1
0
2
1
0
0
6
12
18
20
A.R.X10⁴

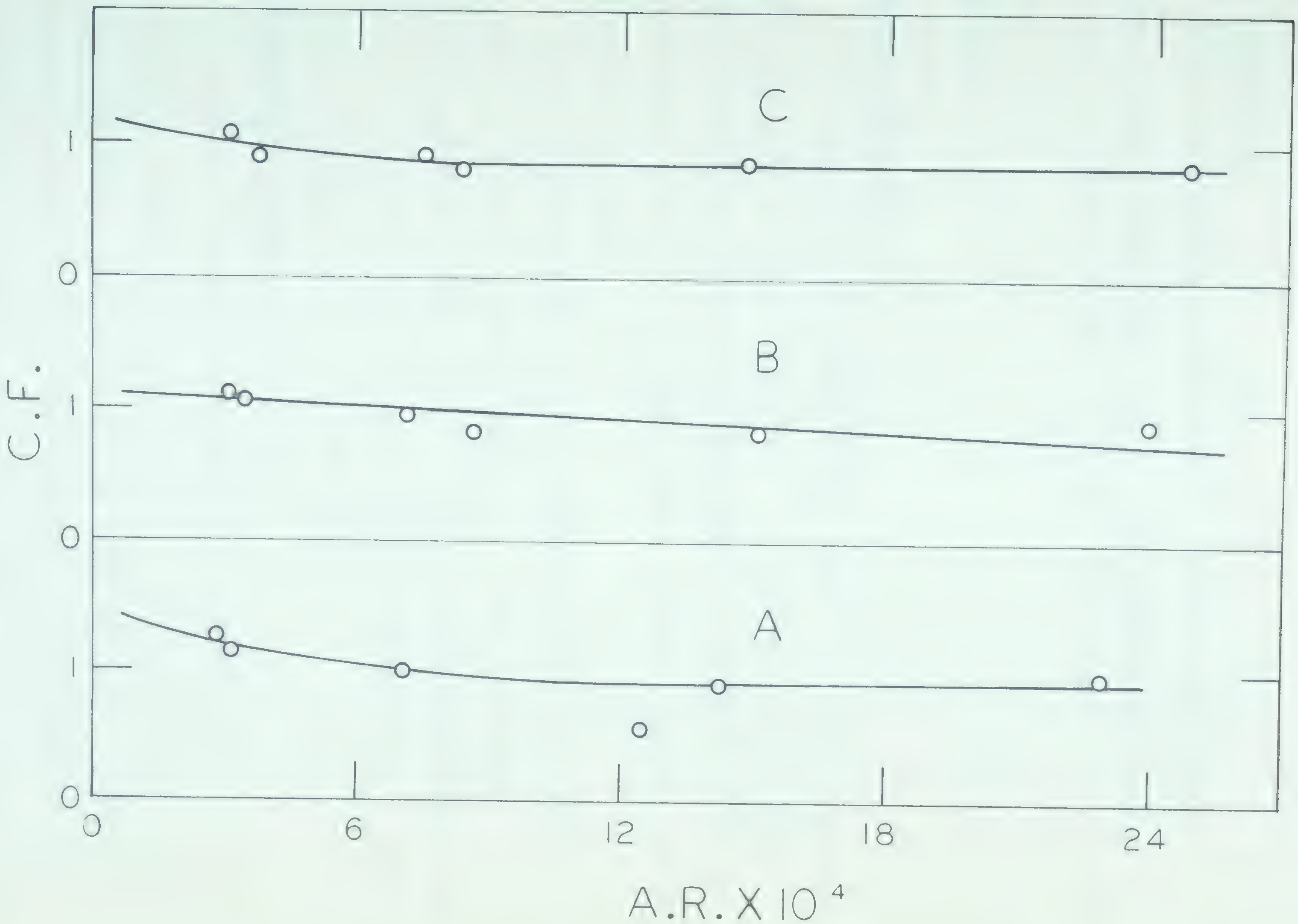
FIGURE III. 34

Calibrations of 5-Hexen-2-one in Benzene Solutions on the Ucon Column.

A.R. = Area of the peak/ Area of cyclohexanone peak.

C.F. = Calibration factor.

	Volume injected (μl)
A.	36
B.	20
C.	10


C
B
A
C.F.
1
0
1
0
1
0
0
6
12
18
24
A.R. X 10 4

was identified to be caproic acid ($G \sim 0.1$; assumed calibration factor ~ 1), by comparison of its retention time with the retention time of an authentic sample of caproic acid.

Peroxides.

Peroxide formation was estimated for the two oxygen solutions and also for pure cyclohexanone. The G values obtained are given in Table III.8. No effort was made to determine the identity of the peroxides formed.

3. C_{12} products.

a. Benzene solutions.

The variation of the yield of total dimer with the concentration of benzene is shown in Figure III.35.A. The G value for total dimer decreases gradually with increasing concentration of benzene, almost all the values being lower than G_{ex} (dashed line). The calibrations given in Figure III.16 were used.

The G values of 2,2'-diketodicyclohexyl[1] and of the dimer D-1, as obtained by analyses on the Silicone grease column, are shown in Figure III.36,A and B. They follow a pattern of decrease similar to that followed by the total dimer, though the decrease seems to be more rapid for the 2,2'-diketodicyclohexyl than for D-1.

b. 2,3-Dimethyl-1,3-butadiene solutions.

In the case of the 2,3-dimethyl-1, 3-butadiene solutions the yield of the total dimer fell very sharply with the increasing electron fraction of the diene. The G value of the total dimer (i.e. dimers of cyclohexanone) seemed to fall to zero before $C_s \sim 2 \times 10^{-3}$. The G values for the total dimer are shown in Figure III.35.B. The three samples with the electron fraction of 2,3-dimethyl-1,3-butadiene equal to 1×10^{-3},

FIGURE III. 35

Total Dimers of Cyclohexanone from Solutions

ϵ_s = Electron fraction of the solute

Dose = 5.92 ± 0.12 (10^{-4} ev/e^-).

Dashed lines refer to G_{ex}

A: Benzene solutions

○ Apiezon L column

△ Silicone grease column

B: 2,3-Dimethyl-1,3-butadiene solutions

○ Apiezon L column

△ Silicone grease column.

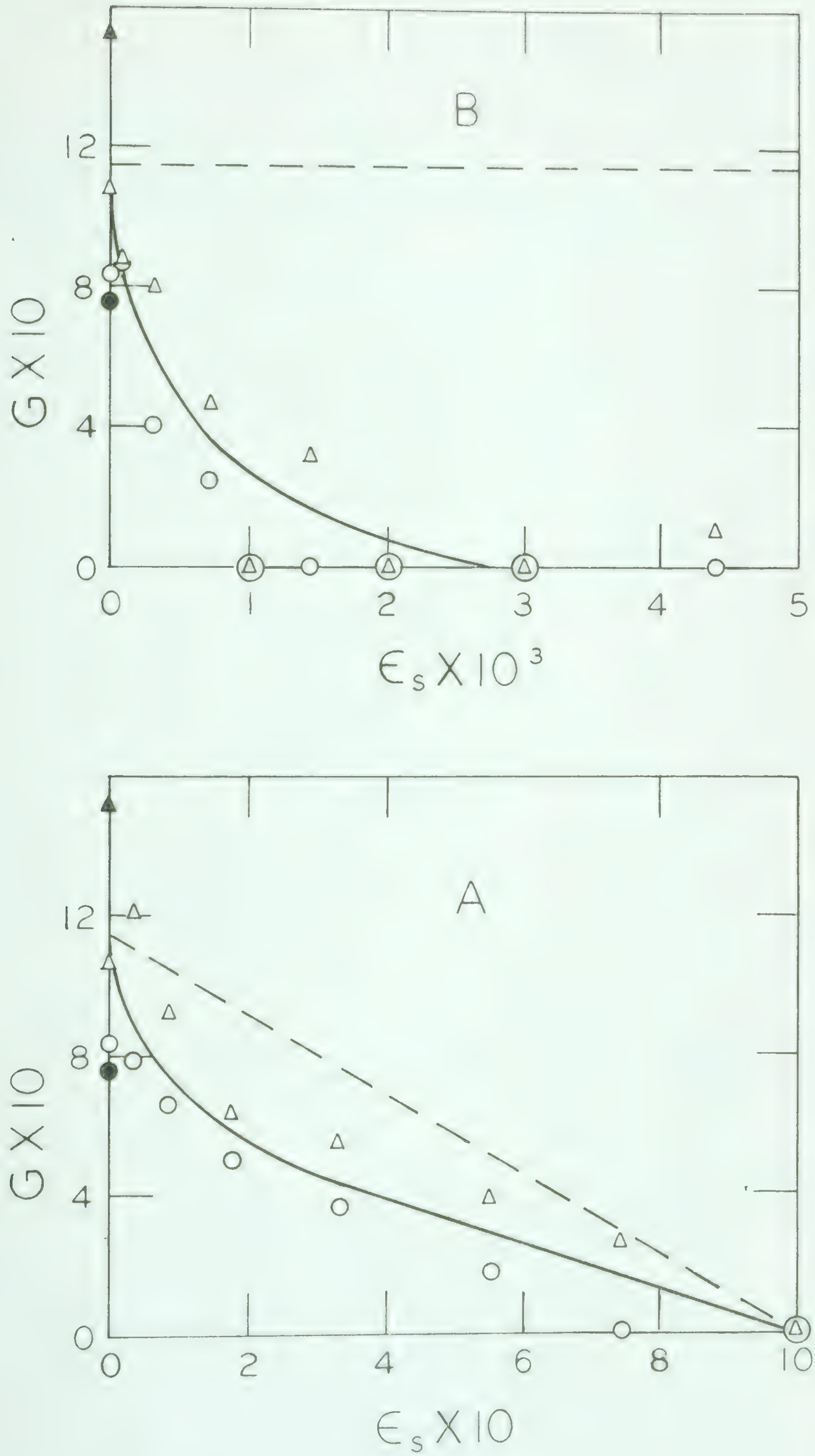

B
G X 10
12
8
4
0
0
1
2
3
4
5
ϵ_s X 10^3
A
G X 10
12
8
4
0
0
2
4
6
8
10
ϵ_s X 10

FIGURE III. 36

Yield of Individual Dimers of Cyclohexanone

ϵ_s = Electron fraction of the solute

Dose = 5.92 $\pm$ 0.12 (10^{-4} ev /e^-)

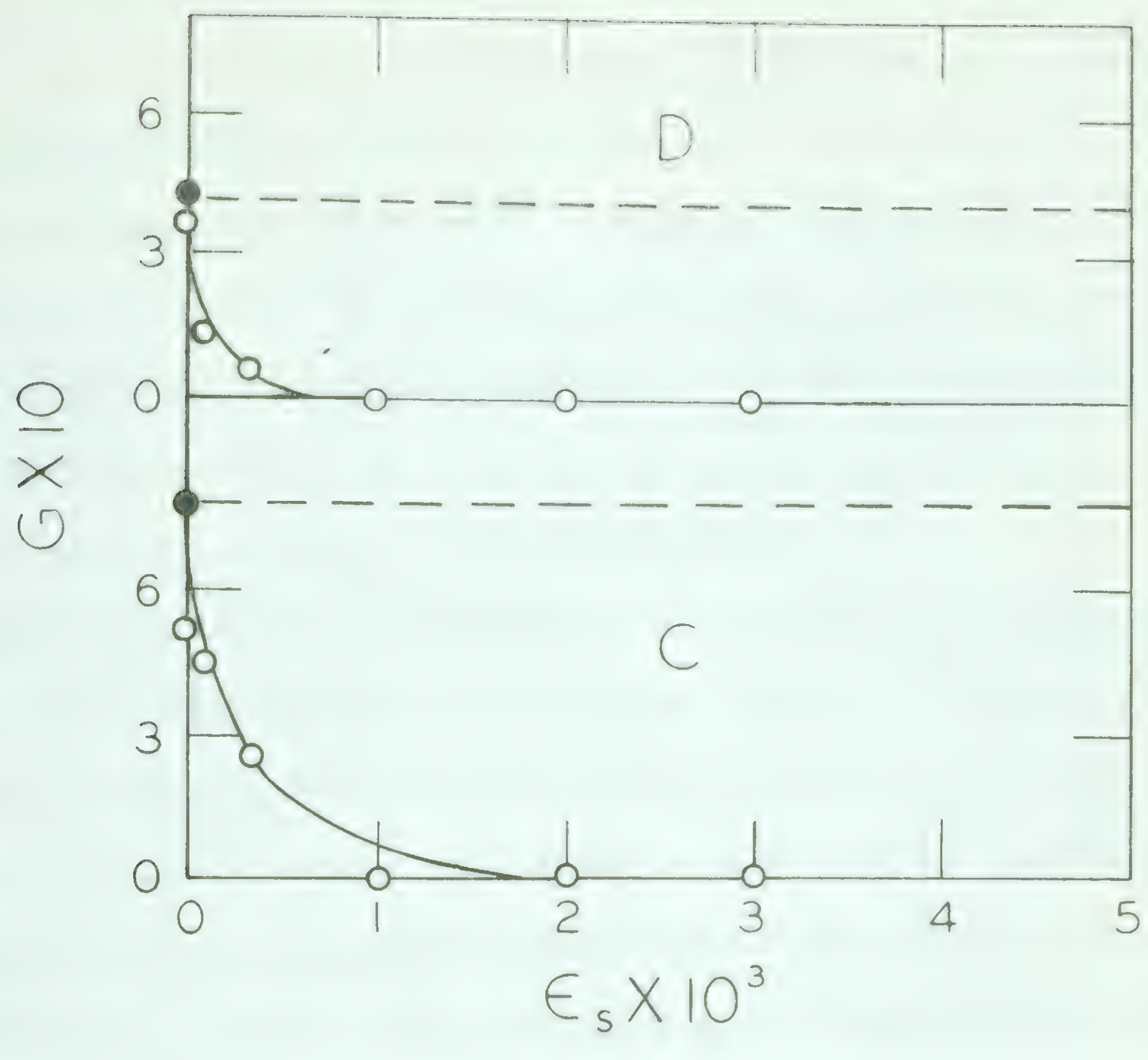
Dashed lines refer to G_{ex}

A: 2,2'-Diketodicyclohexyl; benzene solutions.

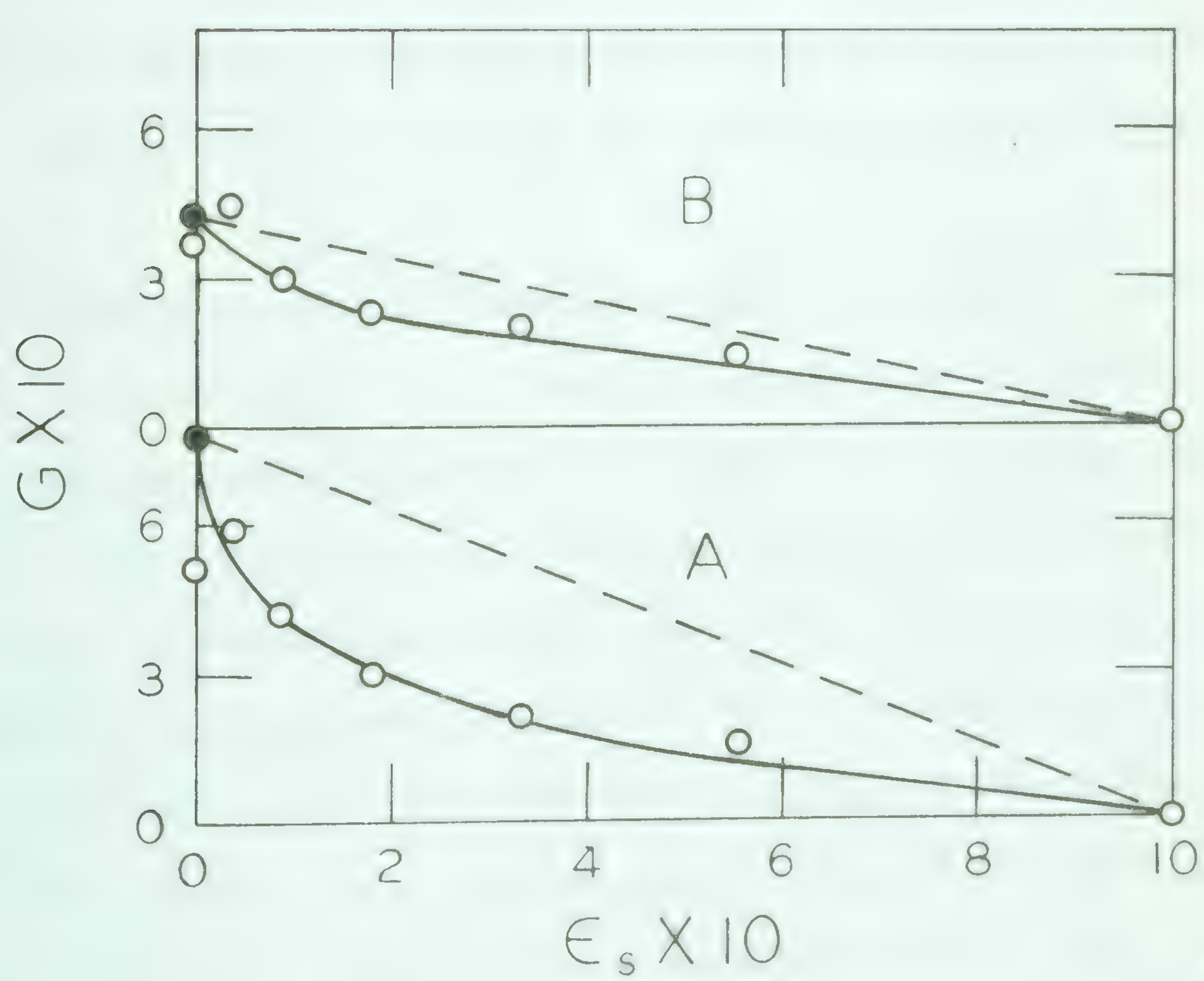
B: Dimer D-1; benzene solutions.

C: 2,2'-Diketodicyclohexyl; 2,3-dimethyl-1,3-butadiene solutions.

D: Dimer D-1; 2,3-dimethyl-1,3-butadiene solutions



D
C
G X 10
0
3
6
0
3
6
0
1
2
3
4
5
$\epsilon_s \times 10^3$



B
A
G X 10
0
3
6
0
3
6
0
2
4
6
8
10
$\epsilon_s \times 10$

2×10^{-3}, and 3×10^{-3} were large samples prepared mainly for polymer analysis and received about half the dose rate ($\sim 2.3 \times 10^{18}$ ev /ml hr) of the other samples ($\sim 5.2 \times 10^{18}$ ev /ml hr) referred to in the same Figure (Fig III.35B). The decrease in the yield of 2,2'-diketodicyclohexyl and the dimer D-1, from the 2,3-dimethyl-1, 3-butadiene solutions is also very rapid and is shown in Figure III.36 (C and D). The calibrations given in Figure III.16 were used.

Pure 2,3-dimethyl-1, 3-butadiene was found to give one big peak and three very small peaks, after the parent peak, by analysis of the radiolysed diene on the Apiezon L and the Silicone grease golumns. By comparison of the retention time of the big peak with the retention time of n-dodecane, the big peak was tentatively identified as the 'dimer' of 2,3 - dimethyl-1, 3-butadiene. The yield of the dimer of 2,3-dimethyl-1, 3-butadiene is shown in Figure III.37.B. It seems to increase very rapidly with increasing diene concentration at first and then seems to remain constant after $\epsilon_s \sim 0.1$. The G values are greater than G_{ex} throughout.

In the 2,3-dimethyl-1, 3-butadiene solutions with $\epsilon_s > 0.02$ many new products seemed to be formed at various concentrations (4 new peaks on the Apiezon L column and 6 new peaks on the Silicone grease column). These peaks appeared in between the main dimer peak of pure 2,3-dimethyl-1, 3-butadiene and the dimer peaks of pure cyclohexanone, by analysis on the Apiezon L and the Silicone grease columns. It is likely that these peaks correspond to 'mixed' dimers formed from the diene and the ketone. The combined yield of these mixed dimers and the dimer of 2-3 dimethyl-1 ,3-butadiene is shown in Figure III.37A. The calibration curves of Figure III.16 have been used for calculation of the G. values (Fig. III.37A). Thus the absolute G values of this Figure

FIGURE III. 37

Dimers that include 2,3-Dimethyl-1,3-butadiene units.

ϵ_s = Electron fraction of the solute.

Dose = 5.92 ± 0.12 (10^{-4} ev /e^-).

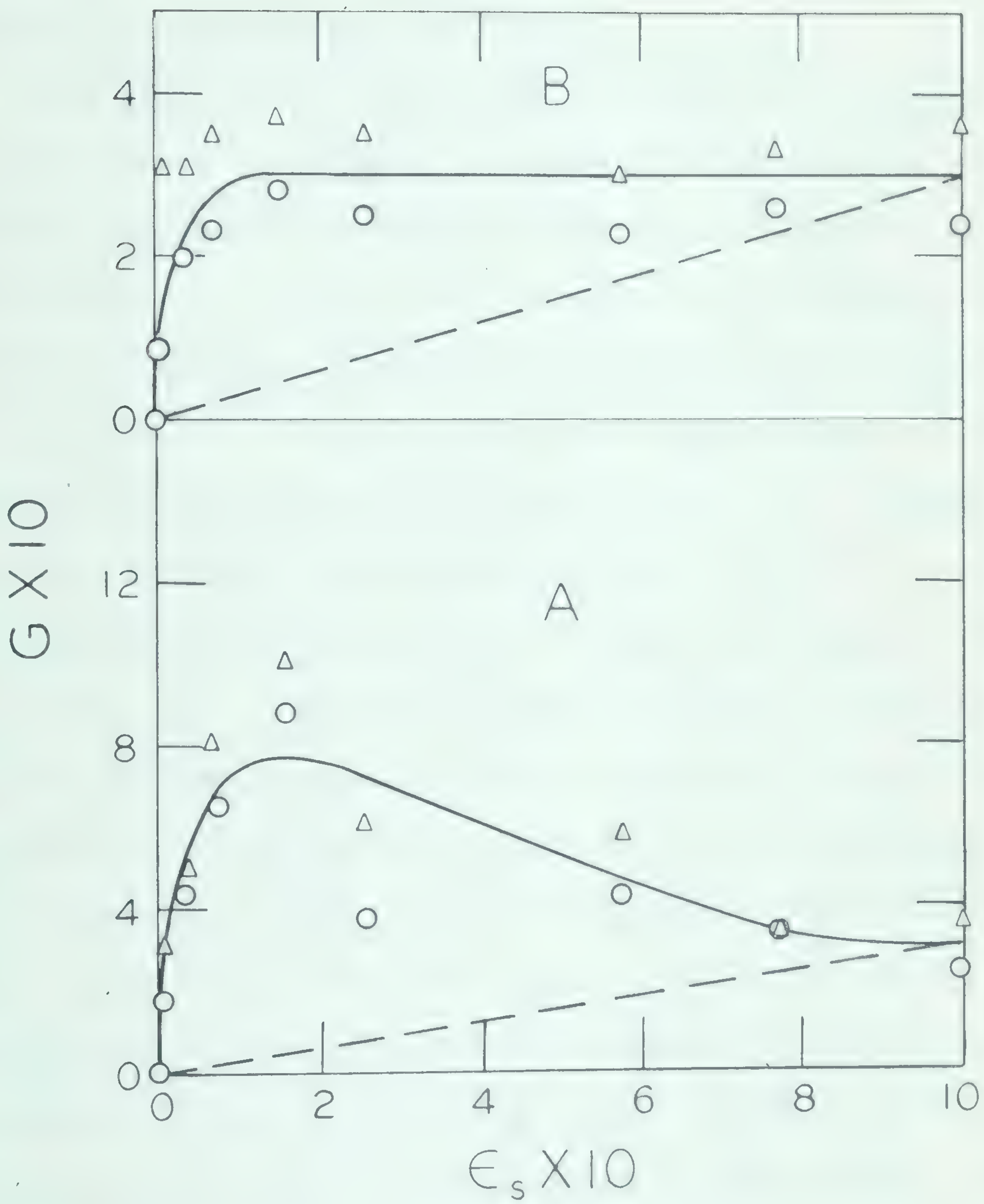
Dashed line refers to G_{ex}

○ Apiezon L column.

△ Silicone grease column.

A: Total dimers, excluding the dimers of cyclohexanone; 2,3-dimethyl-1,3-butadiene solutions.

B: Dimer of 2,3-dimethyl-1, 3-butadiene; 2,3-dimethyl-1, 3-butadiene solutions.


B
A
G X 10
0
2
4
0
4
8
12
0
2
4
6
8
10
ϵ_s X 10

may be wrong by a factor as much as two, but the essential shape of the curves is probably correct.

c. Oxygen solutions.

No C_{12} compounds were observed in the two oxygen containing samples.

4. Consumption of 2,3-dimethyl-1,3-butadiene.

The results given in the preceding sections show that 2,3-dimethyl-1,3-butadiene completely inhibits the formation of cyclohexanol and the dimers and very strongly inhibits the formation of 5-hexenal, at very low concentrations ($\epsilon_5 \sim 2 \times 10^{-3}$). At these low concentrations the amount of 2,3-dimethyl-1,3-butadiene that reacted was measurable(Table III.9). The G (consumption) of the diene from these samples is shown in Figure III.38 and the calibrations are shown in Figure III.32. The G (consumption)of the diene in the maximally inhibited system seems to be about 3.9 (at the dose used the amount of the diene consumed, to give this G value, would correspond to $\epsilon_s = 1.01 \times 10^{-3}$). However, no peaks corresponding to any new products were obtained during analyses of these samples and it was not clear what the products of the diene reaction might be. To investigate the possibility that the main diene reaction product was a polymer, three 20 ml samples with ϵ_s 1×10^{-3} to 3×10^{-3}, were irradiated. The values for G (consumption) of the diene from these samples are shown in Figure III.38 and the amount of the diene remaining is given in Table III.9. No dimers of the ketone or of the diene were observed in these samples. The yields of the polymer are given in Table III.10.

TABLE III.9

Percentage of the Diene Remaining After Irradiation

Dose = 5.92 ± 0.12 (10^{-4} ev /e^-).

Size of the Sample (in ml).	Electron Fraction of the Diene.	Dose Rate (10^{18} ev /ml hr)	% Diene Remaining
2	9.8×10^{-5}	5.2	0
2	3.2×10^{-4}	5.2	0
2	7.2×10^{-4}	5.2	2
20	1.0×10^{-3}	2.3	24
2	1.4×10^{-3}	5.2	32
20	2.0×10^{-3}	2.3	47
20	3.0×10^{-3}	2.3	64
2	4.4×10^{-3}	5.2	86.

FIGURE III. 38.

G (consumption) of 2,3-Dimethyl-1,3-butadiene.

ϵ_s = Electron fraction of the diene.

G = G(consumption) of the diene.

Dose = 5.92 ± 0.12 (10^{-4} ev /e^-)

Dose rate ~ 5.2×10^{18} ev /ml hr.

△ Silicone grease column

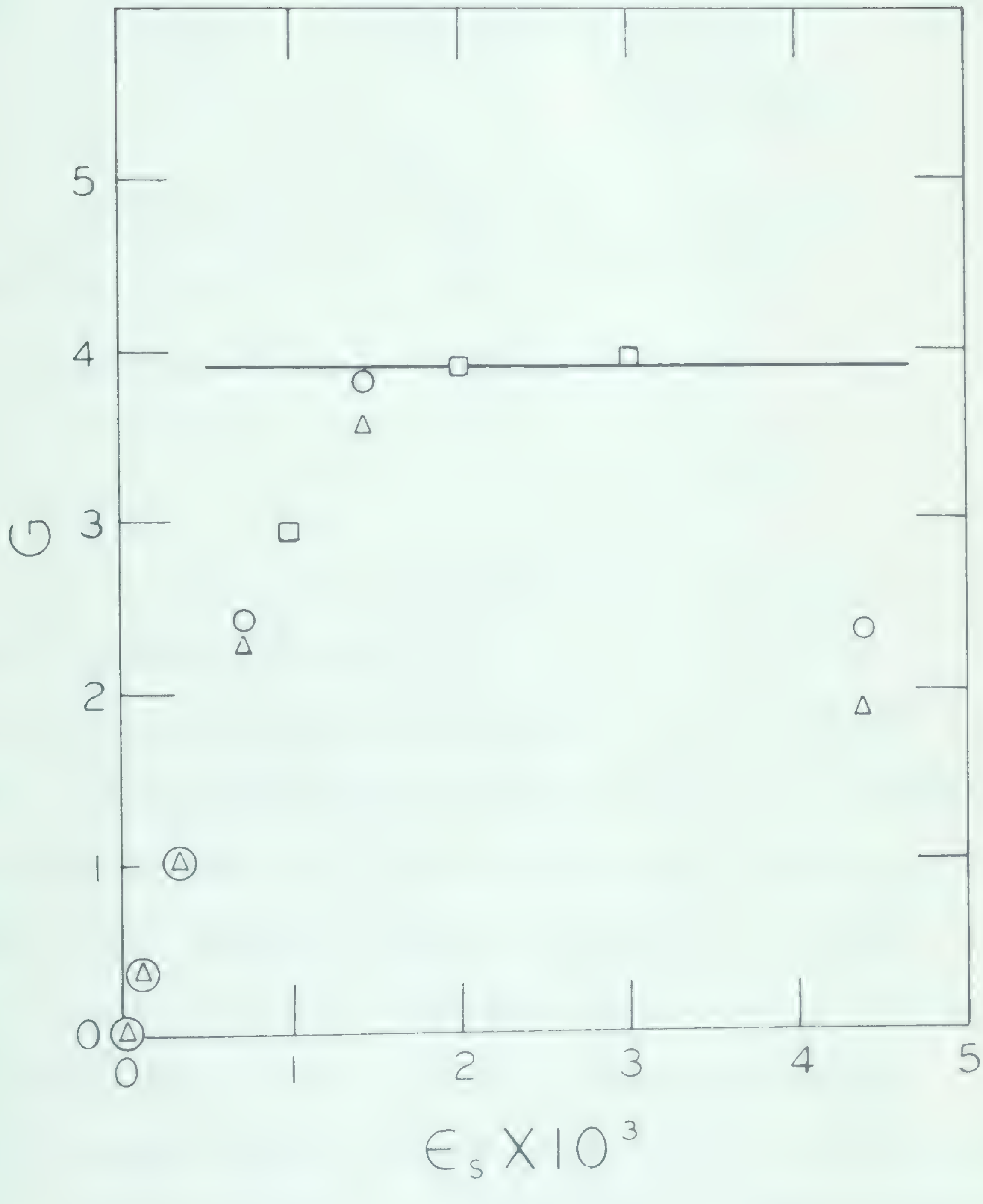
○ Apiezon L column

Dose rate ~ 2.3×10^{18} ev/ml hr.

□ Apiezon L column

Note: (i) The values from the sample with $\epsilon_s = 4.4 \times 10^{-3}$ are less trustworthy since they are based on the measurement of a small difference between two large quantities (diene remaining = 84%, Table III.

(ii) The line represents the maximum value of G (Consumption) of the diene.



G
0
1
2
3
4
5
0
1
2
3
4
5
$\epsilon_s \times 10^3$

TABLE III.10

Estimation of the Diene Consumed and Polymer Formed.

Dose = 5.92 ± 0.02 (10^{-4} ev/e^-).

1 Electron Fraction of the Diene	2 Weight of Polymer (in gm)	3 G(Consumption) of the Diene	4 G(Consumption) of Cyclo-hexanone to form Polymer	5 Total G(Polymer)[a]
0.0	13.0×10^{-3}	0.0	2.2	2.2
1.0×10^{-3}	38.6×10^{-3}	3.0	4.2	7.2
2.0×10^{-3}	38.6×10^{-3}	3.9	3.3	7.2
3.0×10^{-3}	40.0×10^{-3}	4.0	3.5	7.5

a: Sum of values in columns 3 and 4 .

In Table III.10 the G(consumption) of 2,3-dimethyl-1, 3-butadiene is based on gas chromatographic estimation and the G(consumption) of cyclohexanone to form the polymer is calculated from the weight of the polymer with the assumption that all the diene that reacted, formed polymer. The value of total G(polymer) is the sum of the G values of the cyclohexanone and diene units that formed the polymer.

The average molecular weight of the polymer from two samples with $\varepsilon_s = 2.0 \times 10^{-3}$ (dose $\sim 5.9 \times 10^{-4}$ ev /e^-) was found [Pascher, 1963] to be about 400.

IV DISCUSSION

A. General.

A list of the major products of the radiolysis of cyclohexanone is given in Table IV.1, with their initial G values. The yields of the minor products are given in Table IV.2. The yields of most of the minor products could be determined only at high doses and wherever they could be determined at low doses also, the initial G values have been given.

1. Ring opening.

a. Extent of ring opening.

An estimate of the amount of ring opening of cyclohexanone, upon radiolysis, is given by the sum of the G_i values of carbon monoxide and 5-hexenal.

$$G\ (\text{Ring opening}) \simeq 0.48 + 0.85 = 1.33 \quad \text{------------------------} \quad (\text{IV.1})$$

The actual amount of ring opening might be greater than this, depending upon the identity of the dimeric and the polymeric products and upon the mechanism of the formation of 5-hexenal (e.g. if 5-hexenal is being formed by intramolecular disproportionation of the pentamethylene acyl diradical, $\dot{C}H_2(CH_2)_4\dot{C}O$, then since the diradical is also likely to regenerate cyclohexanone by intramolecular combination, the observed yield of 5-hexenal would give too low an estimate of primary ring opening).

An estimate of the amount of primary C-H bond breakage is given by the sum of the G values of cyclohexanol and hydrogen.

$$G\ (\text{Primary C-H bond breakage}) \simeq 0.76 + 0.5 = 1.3 \quad \text{-------------} \quad (\text{IV.2})$$

The actual amount of primary C-H bond breakage might be much greater, depending upon the identity of the dimeric and polymeric products and on the mechanism of the formation of various products.

So, the relative importance of the ring opening as compared to the primary C-H bond breakage is approximately given by the ratio of the expressions IV.1 and I.V. 2 i.e.

$$\frac{\text{Ring Opening}}{\quad} \simeq \frac{1.33}{1.3} = 1.0 \quad \text{-------------} \quad (\text{IV.3})$$

TABLE IV.1

Initial Yields of Major Products.

Product	G_i [a]
Hydrogen	0.76 ± 0.02
Carbon monoxide	0.48 ± 0.02
1 - Pentene	0.22 ± 0.04
5 - Hexenal	0.85 ± 0.15
Cyclohexenone	0.4 ± 0.2
Cyclohexanol	0.5 ± 0.2
Total dimer[b]	1.15 ± 0.45
Polymer	1.8 ± 0.3[c]

a: The possible error, in each case, is estimated visually from the appropriate Figures given in the previous section.

b: The value, $G_i = 1.15$, was obtained from the average of the G values for total dimer obtained from two columns (Silicone grease and Apiezon L columns; see Fig. III.15).

c: This value is obtained by linear extrapolation to zero dose from the values obtained in the region 1.8 - 9.2 (10^{20} ev /ml), and the linear extrapolation might not be valid. (see Fig. III.19).

TABLE IV.2

Yields of Minor Products at[a] 2.5×10^{20} ev/ml.

No.	Product	G^b
1.	Ethane	0.005 ± 0.002
2.	Ethylene	0.12 ± 0.03[c]
3.	Acetylene	0.003 ± 0.001
4.	Propane	0.002 ± 0.001
5.	Cyclopropane	0.013 ± 0.003[c]
6.	Propylene	0.026 ± 0.004[c]
7.	Methyl acetylene	~ 0.002
8.	Allene	~ 0.001
9.	n-Butane	~ 0.0008
10.	1-Butene	0.002 ± 0.001
11.	Butadiene	< 0.001
12.	n-Pentane	0.023 ± 0.004[c]
13.	Cyclopentane	0.04 ± 0.01
14.	2-Pentene	~ 0.004
15.	Peroxides	< 0.3[d]
16.	Polymer ($CHCl_3$ insoluble)	~ 0.1[e]

a: Unless otherwise stated.

b: The possible error is estimated visually from the appropriate Figures given in the previous section.

c: Extrapolated value for zero dose, G_i.

d: On the basis of analysis of two samples, one each at $\sim 2 \times 10^{20}$ ev/ml and $\sim 5 \times 10^{20}$ ev/ml.

e: Average of four samples in the range 1.8 - 9.2 (10^{20} ev/ml).

From the results of the radiolysis of cyclohexane [Ho and Freeman, 1963] the ring opening and primary C-H bond breakage can be estimated. The amount of ring opening of cyclohexane is given approximately by the sum of the G values of 1-hexene (0.43) and cyclohexylhexene-1 (0.19).

$$G \text{ (Ring opening of cyclohexane)} \simeq 0.43 + 0.19 = 0.62 \text{ ---(IV.4)}$$

The actual amount of the ring opening may be somewhat greater depending on the mechanism of the formation of 1-hexene and cyclohexylhexene - 1, (and also on the mechanism of the formation of methylcyclopentane and polymer [Nixon and Thorpe, 1958; Manion and Burton, 1952]).

An estimate of the amount of primary C-H bond breakage is given by $G(H_2)$, which is equal to 5.39. So the ratio of the ring opening to C-H bond breakage for cyclohexane is given by the expression IV.5.

$$\frac{\text{Ring opening}}{\text{Primary C-H bond breakage}} \simeq \frac{0.62}{5.39} = 0.11 \text{ ----------(IV.5)}$$

Similar ratios can also be calculated, on the basis of available results, for methylcyclohexane [Freeman, 1962] and for n-hexane [Dewhurst, 1958; Hardwick, 1960] and are given in expressions IV.6 and IV.7 respectively, and the ratios obtained for the four compounds are given together in Table IV.3, for comparisons.

$$\frac{\text{Ring opening}}{\text{Primary C-H bond breakage}} \text{ (for } C_7H_{14}) \simeq$$

$$\simeq \frac{G(\text{heptene}') + G(\text{heptene}'') + G(\text{Methylcyclohexylheptene})}{G(H_2)} =$$

$$= \frac{0.33 + 0.31 + 0.13}{4.8} = \frac{0.77}{4.8} = 0.16 \text{ ------------------(IV.6)}$$

$$\frac{\text{Primary C-C bond breakage}}{\text{Primary C-H bond breakage}} \text{ (for } C_6H_{14}) \simeq$$

TABLE IV.3

Comparison of Radiolytic Data

Liquid Radiolysed	1	2	3	4
Cyclohexane	0.62	5.39	0.1	10.9 ± 0.6
Methylcyclohexane	0.77	4.80	0.2	9.5 ± 0.7
n-Hexane	1.80	5.28	0.3	9.1
Cyclohexanone	1.33	1.26	1	7.3 ± 2.2

1: Ring opening; except for n-hexane where it refers to primary C-C split; G units.

2: Primary C-H bond breakage; G units.

3: Ratio, 1/2.

4: G (consumption) of the liquid radiolysed, estimated from the G values of products.

$$\simeq \frac{1/2\ G\ (C_1 - C_5 \text{ products}) + 1/2\ G\ (C_7 - C_{11} \text{ products})}{G\ (H_2)} =$$

$$= \frac{1/2\ (2.1 + 1.5)}{5.28} = \frac{1.80}{5.28} = 0.34 \quad \text{(IV.7)}$$

A comparison of the values in column 3 (Table IV.3) shows that the C_6 closed chain in cyclohexane and methlycyclohexane is more 'stable' than the C_6 open chain in n-hexane and that the C_6 closed chain in cyclohexanone is less stable.

It may be argued that the ratio of ring opening to primary C-H bond split, in the radiolysis of cyclohexanone might be higher due to an overall reduction in the amount of the ketone decomposed (per 100 ev) with preferential reduction of C-H bond split. A rough estimate of the amount of substrate consumed during radiolysis for the four C_6 compounds in question can be made on the basis of the observed products, as follows.

$$G(\text{consumption})\text{of } C_6H_{10}O \simeq$$

$$\simeq G(CO) + 2G(C_6H_{11}OH) + 2G(C_6H_8O) + G(\text{5-hexenal}) + 2G\ (\text{Dimer}) +$$

$$+ G(\text{Polymer}) =$$

$$= (0.48 \pm 0.02) + (1.0 \pm 0.4) + (0.8 \pm 0.4) + (0.85 \pm 0.15) +$$

$$+ (2.3 \pm 0.9) + (1.9 \pm 0.3) = 7.3 \pm 2.2 \quad \text{(IV.8)}$$

$$G(\text{consumption}) \text{ of } C_6H_{12} \simeq$$

$$\simeq G(\text{1-hexene}) + 2G\ (\text{cyclohexene}) + 2G(C_{12} \text{ products}) +$$

$$+ G(C_6 \text{ units from} < C_6 \text{ products}) =$$

$$= (0.43 \pm 0.05) + (6.5 \pm 0.4) + (3.9 \pm 0.1) + 0.1 =$$

$$= 10.9 \pm 0.6 \quad \text{(IV.9)}$$

$$G(\text{consumption}) \text{ of } C_7H_{14} \simeq$$

$$\simeq 2G(C_7 \text{ cyclic products}) + G(\text{heptene}' + \text{heptene}'') + 2G(C_{14} \text{ products} +$$

$$+ G\ (C_7 \text{ units from} < C_7 \text{ products}) =$$

$$= (6.96 \pm 0.50) + (0.64 \pm 0.06) + (1.76 \pm 0.14) + 0.1 =$$

$$= 9.5 \pm 0.7 \quad \text{(IV.10)}$$

G(consumption) of $C_6H_{14} \simeq$

$\simeq$ 1/2 G (C_1 - C_5 products) + 3/2 G (C_7 - C_{11} products) +

+ G(C_6 products) + 2G (C_{12} products) =

= 1.05 + 2.25 + 1.8 + 4.0 = 9.1 ------------------------(IV.11)

It may be pointed out here that for such calculations to be correct, the yields of all the products and the exact mechanism of their formation must be known. The values obtained above are, therefore, approximate and are given to show that to a first approximation, the extent of decomposition of each of these compounds, per 100 ev of energy absorbed, is the same. These values are also given in Table IV.3.

It may be concluded, therefore, that the ratio of ring opening to primary C-H bond split is much greater in cyclohexanone than in cyclohexane.

b. Site of ring opening.

If the cyclohexanone ring opens by non preferential C-C bond breakage, upon radiolysis, one would expect the following three diradicals to be formed.

$$\overline{CH_2[CH_2]_4\,CO} \rightsquigarrow \dot{C}H_2(CH_2)_4\,\dot{C}O \text{ ---------------------(IV.12)}$$

$$\rightsquigarrow \dot{C}H_2(CH_2)_3\,CO\,\dot{C}H_2 \text{ -------------------(IV.13)}$$

$$\rightsquigarrow \dot{C}H_2(CH_2)_2\,COCH_2\dot{C}H_2 \text{ -----------------(IV.14)}$$

The diradical formed in reaction IV.12 could give 5-hexenal by intramolecular disproportionation e.g. reaction IV.15

$$\dot{C}H_2(CH_2)_4\,\dot{C}O \longrightarrow CH_2{=}\,CHCH_2\,CH_2\,CH_2\,CHO \text{ -------------(IV.15)}$$

$$\longrightarrow \overline{CH_2\,(CH_2)_4\,CO} \text{ ---------------------(IV.16)}$$

The diradical formed in reaction IV.13 would be resonance

stabilised and could give 5-hexen -2-one by intramolecular disproportionation, and a cyclic ether or cyclohexanone by combination as follows.

$$\dot{C}H_2\,(CH_2)_3\,\overset{O}{\overset{\|}{C}}\,\dot{C}H_2 \longrightarrow CH_2 = CHCH_2\,CH_2\,CO\,CH_3 \text{------------(IV.17)}$$

$$\updownarrow$$

$$\dot{C}H_2(CH_2)_3\,\overset{\dot{O}}{\overset{|}{C}} = CH_2 \longrightarrow CH_2\,(CH_2)_3\,\overset{O}{\overset{|}{C}} = CH_2 \text{------------(IV.18)}$$

$$\longrightarrow CH_2\,(CH_2)_3\,CO\,CH_2 \text{------------(IV.19)}$$

The diradical formed in reaction IV.14 could give either a conjugated or an unconjugated open chain ketone by intramolecular disproportionation or regenerate cyclohexanone by intramolecular combination, as follows.

$$\dot{C}H_2\,CH_2\,CH_2\,COCH_2\,\dot{C}H_2 \longrightarrow CH_3\,CH_2\,CH_2\,COCH = CH_2 \text{------------(IV.20)}$$

$$\longrightarrow CH_2 = CH\text{-}CH_2\,COCH_2\,CH_3 \text{------------(IV.21)}$$

$$\longrightarrow CH_2 = CH_2\,CH_2\,COCH_2\,CH_2 \text{------------(IV.22)}$$

No products corresponding to reactions IV.17, IV.18, IV.20 or IV.21 were seen to be formed upon radiolysis of cyclohexanone. However, the possibility of the formation of diradicals according to reactions IV.13 and IV.14 cannot be entirely ruled out since the composition of the C_{12} products and the polymer is not known.

It would seem, therefore, that on the basis of the observed yields of the C_6 products and CO, the C-C bonds on the oxygen bearing carbon in the molecule are more susceptible to fission than the other C-C bonds. This is consistent with the view that the presence of carbonyl group in an organic molecule causes a weakening of the other bonds on the oxygen bearing carbon, the latter being also evident from a comparison of available bond dissociation energies [Cottrell, 1958]

shows that the C-C bond in acetone is weaker than the C-C bond in propane [$D(CH_3CO - CH_3) = 72$ kcal/mole; $D(C_2H_5 - CH_3) = 85$ kcal/mole]. Similarly, the C-C bond in acetaldehyde is weaker than the C-C bond in ethane [$D(CH_3 - CHO) = 75 \pm 5$ kcal/mole; $D(CH_3 - CH_3) = 83$ kcal/mole] and the C-H bond in formaldehyde is weaker than the C-H bond in methane [$D(H-CHO) = 75 \pm 5$ kcal/mole; $D(H - CH_3) \backsim 101$ kcal/mole].

The bond dissociation energies of the various bonds in cyclohexanone are not known. However, analogies can be drawn from the above mentioned cases and it can be tentatively concluded that the C-C bonds at the carbonyl carbon would be weaker than the other C-C bonds. The fact that 5-hexenal and CO are the major products due to ring opening in the radiolysis of cyclohexanone is consistent with this conclusion. Katayama and coworkers have found CO to be a major product in the radiolysis of cyclopentanone [Katayama et al, 1962], which is consistent with the view just expressed.

A comment may be made here about the lower apparent amount of C-C bond fission in cyclic compounds than in open chain compounds. In the open chain compounds two separate radicals would be formed upon C-C bond breakage and, except for the Cage effect [Franck and Rabinowitch, 1934], they are relatively free to diffuse away from each other. On the other hand, in cyclic compounds, a diradical would result upon breakage of the ring, whose two ends are held together by the rest of the molecule, thus increasing the probability of the combination of the two ends to regenerate the original molecule. It may be remarked here that some or all of the differences in the extent of the observed ring opening in cyclohexanone as compared to that in cyclohexane might be due to a difference in the amount of regeneration of the substrate by ring closure of the diradical concerned.

2. Comparison of radiolysis and photolysis of cyclohexanone.

Carbon monoxide is a major product of both liquid and vapour phase photolysis of cyclohexanone [Saltmarsh and Norrish, 1935; Bamford and Norrish, 1938; Benson and Kistiakowsky, 1942; Blacet and Miller, 1957; Srinivasan, 1959]. The present work shows that it is also a major product of the radiolysis of liquid cyclohexanone. Ethylene, propylene, 1-pentene and cyclopentane are formed in the radiolysis of the ketone. They were found to be important products in the vapour phase photolysis of cyclohexanone by the above mentioned workers. The liquid phase photolysis work was more limited [Srinivasan, 1959] and these products do not seem to have been looked for.

Srinivasan found that 5-hexenal is a product of the vapour and liquid phase photolyses of cyclohexanone [Srinivasan, 1959]. He also showed that the 5-hexenal formation was 3.7 times greater than that of carbon monoxide in the vapour phase and was about 11 times greater in the liquid phase. The radiolytic yield of 5-hexenal from liquid cyclohexanone is only about twice the radiolytic yield of carbon monoxide.

Polymer formation in the vapour phase photolysis of cyclohexanone has been reported and Blacet and Miller suggested that the polymer formation increases at lower wavelengths [Benson and Kistiakowksy, 1942; Blacet and Miller, 1957]. Polymer is found to be a major product in the radiolysis of the ketone.

Hydrogen, cyclohexanol, cyclohexenone and dimer are major products of the radiolysis and their formation has not been reported in the photolytic studies but this may be due to lack of effort to find them. It may be pointed out that the C-H bond energy in the ketone is likely to be $\sim$95 kcal/mole [D (iso C_3H_7 - H) = 94 $\pm$ 2 kcal/mole; Cottrell, 1958] so that the energy of a light quantum is not sufficient to break the C-H bond where light of wavelength greater than about 300 $m\mu$ has

been used. In the case of cyclopentanone it has been reported that hydrogen is not a product when the ketone is photolysed with light of 313mμ [Katayama et al, 1962]. Photolytic formation of cyclohexanol from cyclohexanone has been suggested [Mayo, 1960] but it is not certain whether it has been observed as a product. A large number of minor products are formed in the radiolysis of the ketone e.g. acetylene, propane, cyclopropane, etc., which have not been reported in the photolytic studies.

It may be concluded that the energy states involved in the radiolytic formation of hydrogen are higher than the energy states involved in photolysis. The other products of radiolysis that have not been reported in photolysis of the ketone may also have a significant contribution from energy states higher than those involved in photolysis. The difference in the relative yields of 5-hexenal and carbon monoxide in the photolysis and in the radiolysis of liquid cyclohexanone is also indicative of the involvement of different excited states in the two systems. However, it is difficult to say whether these different states mainly differ from each other in their electronic levels or in their vibrational levels.

B. Products Involving C-H Bond Rupture.

The effort in this and subsequent sections is limited to the consideration of some of the more probable mechanisms from the point of view of their consistency, or lack of it, with the experimental results obtained. Although certain mechanisms seem to be favoured, the data do not allow definite conclusions to be drawn.

1. Hydrogen.

The radiolytic formation of hydrogen from various organic compounds has been widely investigated and discussed [e.g. Manion and Burton, 1952; Freeman, 1960; Dyne and Jenkinson, 1962; Hardwick, 1962]. The G value of hydrogen from cyclohexanone seems to decrease slightly with increasing dose (Fig III.2.A). The decrease is most probably due to secondary reactions involving the products.

Benzene and 2,3-dimethyl-1,3-butadiene decrease the radiolytic yield of hydrogen from cyclohexanone (Fig. III.22). The decrease in the yield of hydrogen might either be due to a scavenging mechanism involving the precursors of hydrogen (e.g. H atoms) or it might be due to protection of the ketone by an activation transfer mechanism, which reduces the initial decomposition of the ketone itself, or it might be a combination of the two. In the following discussion the 'scavenging-type' mechanisms and the 'activation transfer-type' mechanisms are considered separately. It is assumed in the following treatments that the yield of hydrogen from the direct irradiation of the inhibitor is proportional to the electron fraction of the inhibitor.

a. Mechanism 1 (Scavenging - type).

$$C_6H_{10}O \xrightarrow{I_1} C_6H_{10}O^* \text{ ---------------------- } (1)$$

$$C_6H_{10}O^* \longrightarrow H + (C_6H_9O). \text{ ----------------- } (2)$$

$$H + C_6H_{10}O \longrightarrow H_2 + (C_6H_9O). \text{ ----------------- } (3)$$

$$\longrightarrow (C_6H_{11}O). \text{ -------------------- } (4)$$

$$H + In \longrightarrow (HIn). \text{ ----------------------- } (5)$$

$$\longrightarrow H_2 + R_1. \text{ -------------------- } (6)$$

The inhibitor is represented by In (benzene or 2,3-dimethyl-1,3-butadiene in the present case) and R_1. represents the free radical derived from the inhibitor.

By the usual steady state treatment of Mechanism 1 the following expressions (IV.23 - IV.25) are obtained.

$$\frac{d\,[H]}{dt} = k_2[C_6H_{10}O^*] - (k_3 + k_4)\,[H]\,[C_6H_{10}O] -$$

$$- (k_5 + k_6)\,[H]\,[In] = 0 \text{ ------------------------------ } (IV.23)$$

$$\frac{d\,[C_6H_{10}O^*]}{dt} = I_1 - k_2[C_6H_{10}O^*] = 0 \text{ -------------------------- } (IV.24)$$

$$\frac{d\,[H_2]}{dt} = \frac{k_3 I_1}{k_3 + k_4}\left\{ \left. 1 + \frac{k_6\,[In]}{k_3\,[C_6H_{10}O]} \middle/ 1 + \left[\frac{(k_5 + k_6)\,[In]}{(k_3 + k_4)\,[C_6H_{10}O]}\right] \right. \right\} \text{--} (IV.25)$$

The rate of formation of $C_6H_{10}O^*$ is represented by I_1, which is assumed to be proportional to the electron fraction of cyclohexanone (ϵ_c) in the samples studied, and $G(C_6H_{10}O^*) = AI_1$, where A is a proportionality constant that includes the irradiation dose rate.

Expression IV.25 can be rearranged to IV.26.

$$\left\{1 + \frac{k_6\ [In]}{k_3\ [C_6H_{10}O]}\right\} \frac{(k_3/k_3 + k_4)\ I_1}{d[H_2]/\ dt} = 1 + \frac{(k_5 + k_6)\ [In]}{(k_3 + k_4)\ [C_6H_{10}O]} \text{ --- (IV.26)}$$

Expression IV.26 can be written in a more general form as follows.

$$\left\{1 + y\ \frac{[In]}{[C_6H_{10}O]}\right\} \rho_1 = 1 + z\ \frac{[In]}{[C_6H_{10}O]} \text{ ---------------------- (IV.27)}$$

where, $y = k_{6}/k_{3}$

$$\rho_1 = \frac{(k_3/k_3 + k_4)\ I_1}{d[H_2]\ /\ dt}$$

and $z = \dfrac{k_5 + k_6}{k_3 + k_4}$

for Mechanism 1.

Now, ρ_1 can be obtained from the experimentally observed yields of hydrogen as follows.

From steps (1) to (4) of Mechanism 1 it can be seen that

$$G_i(H_2) = \frac{k_3}{k_3 + k_4}\ G[C_6H_{10}O^*] = \frac{k_3}{k_3 + k_4}\ AI_1 = 0.76$$

Therefore, $G_{ex}(H_2)c$ from the cyclohexanone in the solution =

$$= \frac{k_3}{k_3 + k_4} AI_1\ \epsilon_c = 0.76\ \epsilon_c \text{ ---------------------- (IV.28)}$$

The rate of formation of hydrogen, $d[H_2]/dt$, does not include the hydrogen produced by the direct radiolysis of the inhibitor, so that

$$A \frac{d[H_2]}{dt} = G_{obs}(H_2) - G_{In}(H_2)\, \epsilon_{In} \quad \text{------------------} \quad (IV.29)$$

where $G_{obs}(H_2) = G(H_2)$ from the solutions;

$G_{In}(H_2) = G(H_2)$ from pure inhibitor;

and $\epsilon_{In} =$ electron fraction of the inhibitor.

Thus, f_1 of expression IV.27 is given by expression IV.30.

$$f_1 = \frac{G_{ex}(H_2)_c}{G_{obs}(H_2) - G_{In}(H_2) \quad {}_{In}} \quad \text{---------------} \quad (IV.30)$$

If y of the expression IV.27 were known, the left hand side of that expression could be plotted against $[In]/[C_6H_{10}O]$, and a straight line should be obtained with an intercept of unity and slope = z, if Mechanism 1 were applicable. In the present case, various arbitrary values of y were assumed (0 to 5) and several plots, according to the expression IV. 27, were made to see if a straight line with an intercept of unity could be obtained.

When plots were made using the value of $G_{ex}(H_2)_c = 0.76\ \epsilon_c$, an intercept of unity could not be obtained, even when a straight line was obtained. The value of $G\ (H_2)$ from pure cyclohexanone at the dose used in the inhibition experiments (5.9×10^{-4} ev/e^- or $\backsim 1.9 \times 10^{20}$ev/ml) is equal to 0.71. The use of $G_{ex}(H_2)_c = 0.71\ \epsilon_c$ gave an intercept of unity for the straight line plots. So, in the following treatment this value has been used for the caluculation of the values of f . This involves the assumption that the secondary products of radiolysis have a similar effect on the yield of hydrogen in the pure phase and in the solutions.

It may be pointed out here that expressions similar to the expression IV.27, where f is essentially a function of $[In]/[C_6H_{10}O]$, can also be obtained from mechanisms other than Mechanism 1. Two such mechanisms are given in Appendix A, which involve 'scavenging' of positive charges (Mechanism 3) and electrons (Mechanism 4) by the inhibitor.

(i) Benzene solutions.

For the benzene solutions the best straight line was obtained with $y = 1$ (Fig IV.1). A comparison of the points obtained with $y = 0$ and $y = 2$ with those obtained with $y = 1$ indicates that the kinetic plot, according to the expression IV.27, is not as sensitive to the variation in the value of y as might be desired. This may either be due to the inapplicability of the scavenging - type mechanisms or may be due to lack of adequate precision of the data.

The values $y = 1$ and $z = 3$ would mean that (i) the overall rate constant for the reaction of the scavengable species with benzene was about three times greater than the corresponding rate constant for the reaction of the same species with cyclohexanone; (ii) the rate constants for hydrogen abstraction by an H atom from benzene and from cyclohexanone had the same value (Mechanism 1), or that about a third of the benzene ions produced by positive charge or electron scavenging reactions result in the formation of hydrogen (Mechanism 3 and 4 respectively).

Since the bond dissociation energy of the C-H bond in $C_6H_{10}O$ is likely to be ~ 95 kcal/mole [D (iso C_3H_7 —— H) $= 94 \pm 2$ kcal/mole] whereas the C-H bond dissociation energy for C_6H_6 is ~ 102 kcal/mole [Cottrell, 1958], k_6 would not be expected to be equal to k_3 (Mechanism 1). Thus Mechanism 1 seems to be inapplicable in the present case.

The ionization potential of cyclohexanone (9.14 ev) is lower than that of benzene (9.25 ev) [Watanabe et al, 1962]. Thus reaction 15 of

FIGURE IV.1

Kinetic Plot for Scavenging - Type Mechanism.

In = Benzene.

$$R_1 = \left(1 + y \frac{[In]}{[C_6H_{10}O]}\right) \rho_1$$

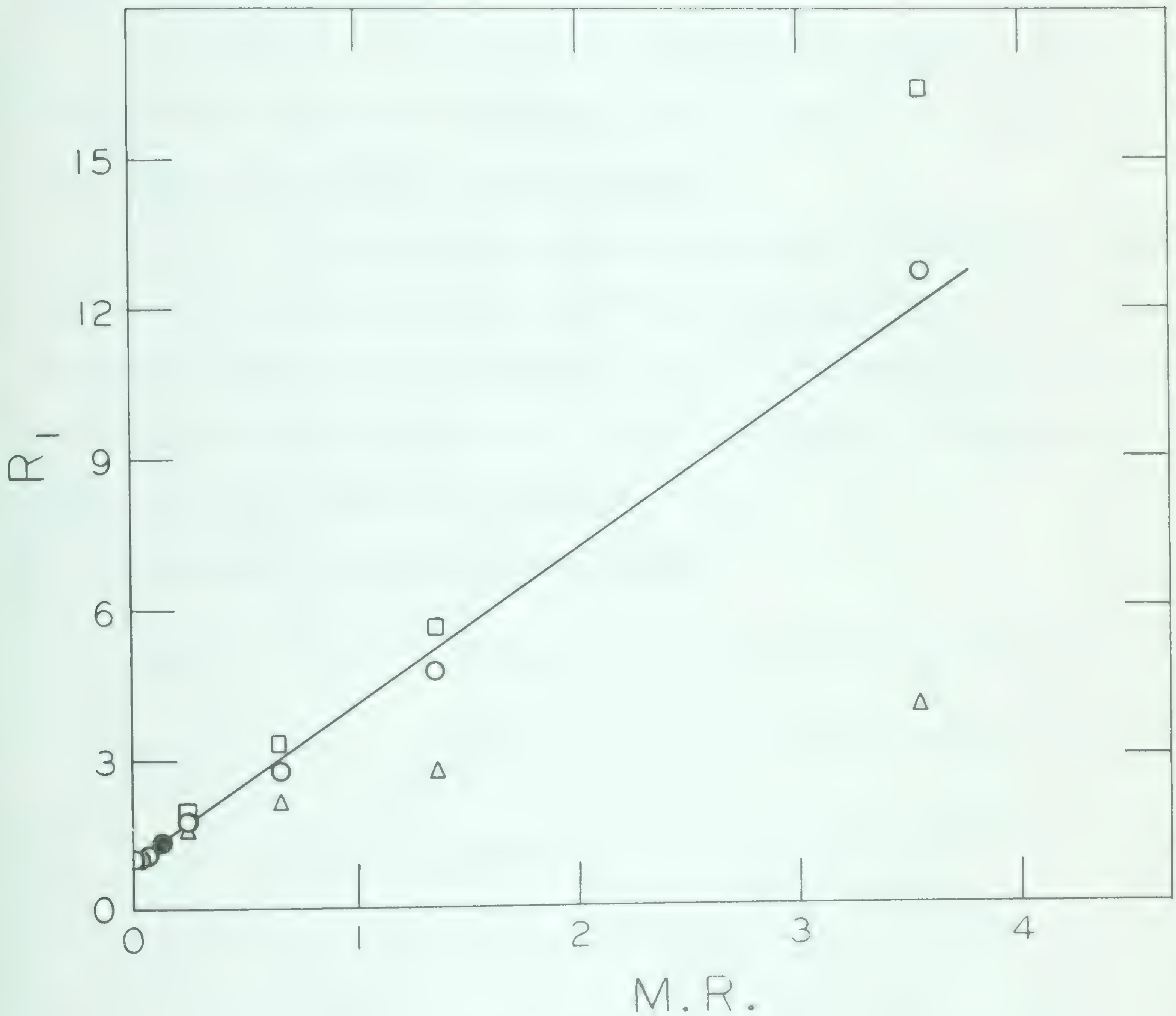
$$M.R. = \frac{[In]}{[C_6H_{10}O]}$$

● Represents the point from which all other points were normalized. Triangles and squares are not shown for M.R. $<$ 0.12 because they differed negligibly from the circles.

△ y = 0

○ y = 1

□ y = 2



15
12
9
6
3
0
R_I
0
1
2
3
4
M.R.

Mechanism 3 (Appendix A) would not be expected to occur [Smyth, 1931], unless $C_6H_{10}O^+$ were an excited ion. Even if reaction 15 did occur, the requirement that about 1/3 of the molecules of benzene that gain positive charge should give H_2 would seem unjustifiable since $G(H_2)$ from pure benzene is very low (0.038). Thus Mechanism 3 seems to be inapplicable in this case.

No conclusions can be drawn about Mechanism 4 since the electron affinities of benzene and cyclohexanone are not known.

(ii) 2,3-Dimethyl-1,3-butadiene solutions.

For the 2,3-dimethyl-1,3-butadiene solutions a satisfactory straight line plot could not be obtained (Fig IV.2). This may either be due to lack of adequate precision of the present data or due to the inapplicability of such simple mechanisms (Mechanisms 1,3 and 4) to explain the radiolytic production of hydrogen from the ketone.

b. Mechanism 2 (Activation transfer-type.

$$C_6H_{10}O \overset{I_2}{\rightsquigarrow} C_6H_{10}O^* \qquad (7)$$

$$C_6H_{10}O^* \longrightarrow \text{ч} \rightarrow H_2 + P_1 \qquad (8)$$

$$C_6H_{10}O^* + In \longrightarrow C_6H_{10}O + In^* \qquad (9)$$

$$In^* \longrightarrow \text{ч} \longrightarrow H_2 + P_2 \qquad (10)$$

$$In^* \longrightarrow In \qquad (11)$$

In this mechanism ч (pronounced 'chay') could be a hot hydrogen atom, an activated complex prior to the formation of H_2, or some such entity. Reactions 8 and 10 could each involve more than one molecule and both could involve more steps than one. Products P_1 and P_2 may each refer to more than one entity. The inhibitor is represented by In, and I_2 has a meaning

FIGURE IV.2

Kinetic Plot for Scavenging - Type Mechanism.

In = 2,3- Dimethyl-1,3 - butadiene.

$$R_1 = \left(1 + y \frac{[In]}{[C_6H_{10}O]}\right) \rho_1$$

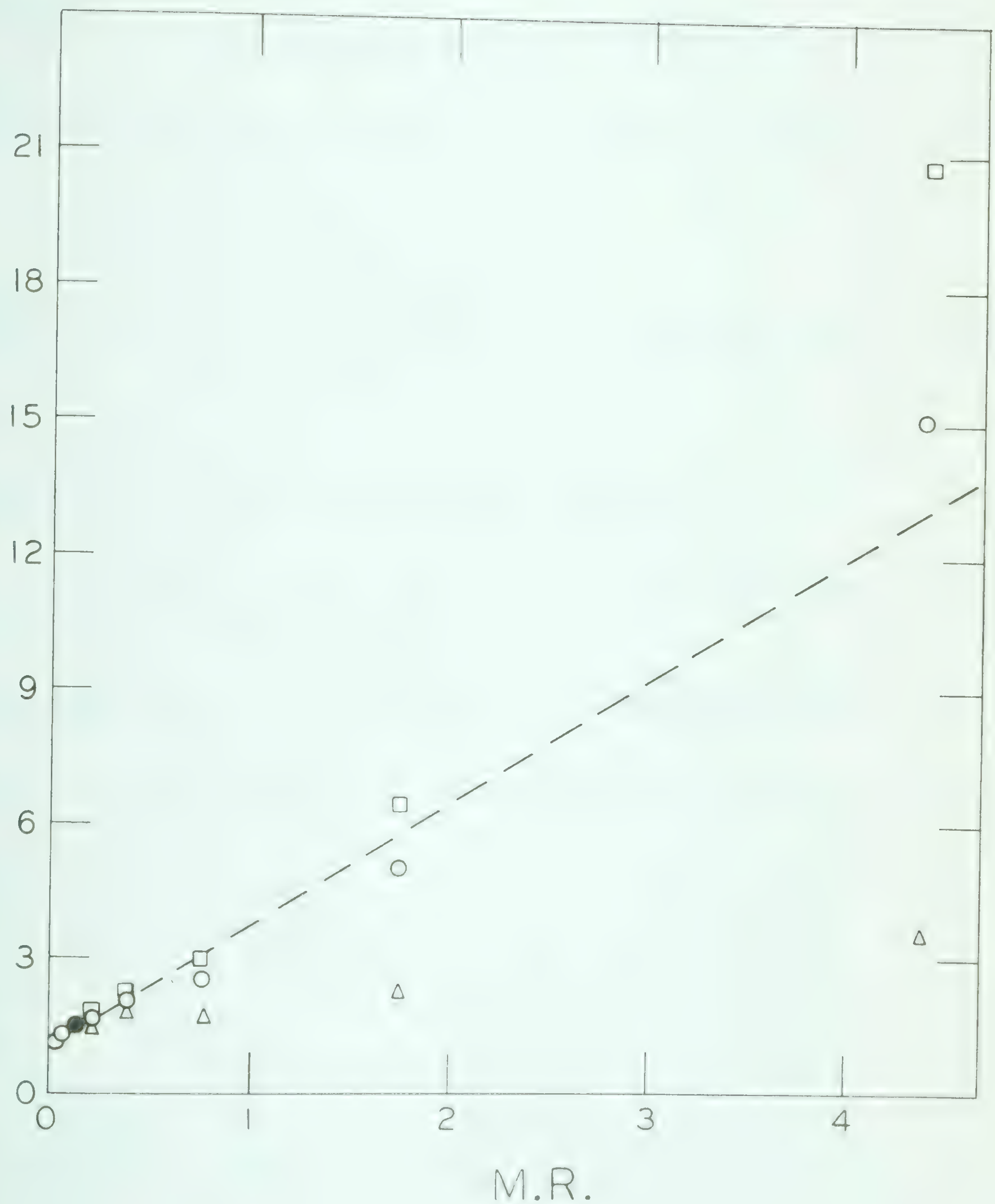
$$M.R. = \frac{[In]}{[C_6H_{10}O]}$$

Represents the point from which all other points were normalized. Traingles and squares are not shown for M.R.$<$0.13 because they differed negligibly from the circles.

$\triangle$ y = 0

$\bigcirc$ y = 1

$\square$ y = 2



21
18
15
12
9
6
3
0
0
1
2
3
4
R_1
M.R.

similar to that of I_1 in Mechanism 1.

By the usual steady state treatment of Mechanism 2, the following expressions are obtained.

$$\frac{d[C_6H_{10}O^*]}{dt} = I_2 - k_8[C_6H_{10}O^*] - k_9[C_6H_{10}O^*]\,[In] \text{ ------------------ } (IV.31)$$

$$\frac{d[In^*]}{dt} = k_9[In]\,[C_6H_{10}O^*] - (k_{10} + k_{11})\,[In^*] \text{ ------------------ } (IV.32)$$

$$\frac{d[H_2]}{dt} = I_2 \left\{ \frac{1 + \dfrac{k_9 k_{10}}{k_8(k_{10} + k_{11})}[In]}{1 + \dfrac{k_9}{k_8}[In]} \right\} \text{ ---------------------- } (IV.33)$$

Expression IV.33 may be rearranged to the following

$$\left(1 + \frac{k_9\, k_{10}\,[In]}{k_8(k_{10} + k_{11})}\right) \frac{I_2}{d[H_2]/dt} = \left(1 + \frac{k_9}{k_8}[In]\right) \text{ -------- } (IV.34)$$

which may be written in a more general form as expression IV.35.

$$(1 + v\,[In])\,\rho_2 = (1 + u\,[In]) \text{ ---------------------------- } (IV.35)$$

where

$$v = \frac{k_9\, k_{10}}{k_8\,(k_{10} + k_{11})}$$

$$u = \left(\frac{k_9}{k_8}\right)$$

and $$\rho_2 = \frac{I_2}{d[H_2]/dt} = \frac{G_{ex}\,(H_2)_c}{G_{obs}\,(H_2) - G_{In}(H_2)\,\epsilon_{In}}$$

for Mechanism 2.

f_2 can be obtained from the experimentally observed values, and the data can be plotted according to the expression IV.35, as before. In the present case various arbitrary values of v were assumed (0 to 5) and several plots were made to see if a straight line with an intercept of unity could be obtained. Here also it was found necessary to use $G_{ex}(H_2)c = 0.71\ \epsilon_c$ in the expression for f_2 to get the unity intercept in the plots.

An expression similar to the expression IV.35 can also be obtained from another mechanism (Mechanism 5, Appendix B).

(i) <u>Benzene solutions.</u>

For values from the benzene solutions the best straight line plot was obtained with v = 0 which is shown in Figure IV.3. A plot with

v = 0 which is shown in Figure IV.3. A plot with v = 0.5 is shown for comparison (Fig IV.3). The value v = 0 means that benzene does not produce hydrogen subsequent to the protection of cyclohexanone by activation transfer (Mechanisms 2 and 5).

The slope of the straight line (Fig IV.3) gives u = 0.2 l/mole.

Thus Mechanisms 2 and 5 are not inconsistent with the present results. Many previous workers [e.g. Manion and Burton, 1952] have made the assumption that benzene does not produce hydrogen subsequent to energy transfer from another component during radiolyses of their binary solutions, which is equivalent to v = 0 as obtained here.

A general case of energy transfer in a binary system was considered by Manion and Burton where they pointed out that the relative values of excitation potentials, E_A and E_B, of two substances A and B are not set by their ionization potentials, I_A and I_B and that either of the reactions

$$A^* + B \longrightarrow A + B^* \text{ ---------------------- } \quad (IV.36)$$

$$A + B^* \longrightarrow A^* + B \text{ ---------------------- } \quad (IV.37)$$

IV.36 or IV.37 can occur

FIGURE IV. 3

Kinetic Plot for Activation Transfer - Type Mechanism.

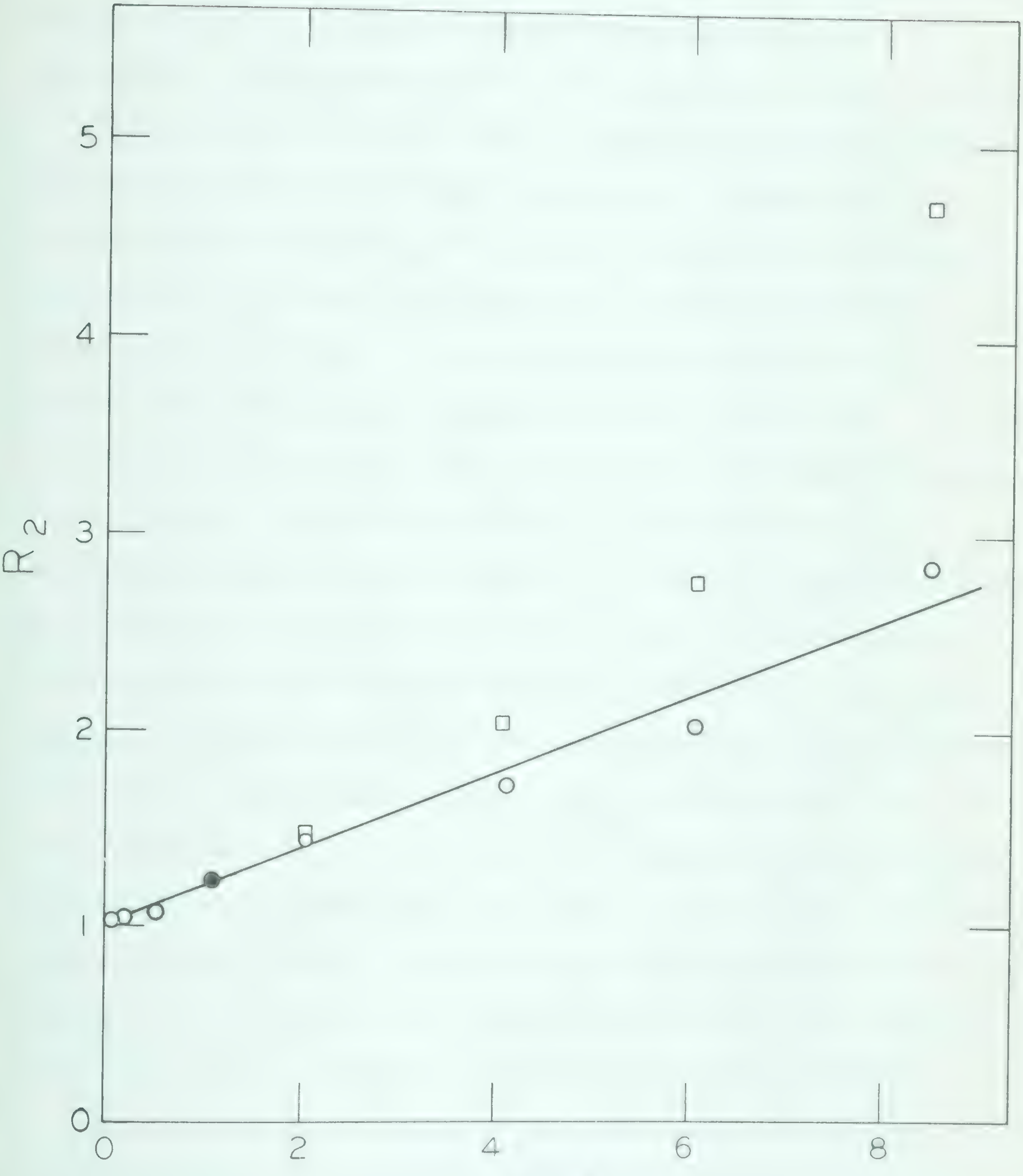
In = Benzene.

$$R_2 = (1 + v\,[In])\rho_2$$

● Represents the point from which all other points were normalized. Squares are not shown for [In] $<$ 1.1 because they differed negligibly from the circles.

○ v = 0

□ v = 0.5



R2
5
4
3
2
1
0
0
2
4
6
8
[In]

depending on the relative heights of the energy levels involved [Manion and Burton, 1952].

In another communication [Burton et al, 1952] it was contended that for the most part, the excited molecules formed initially in the radiolysis are in the lowest excited states. Then in the work on solutions of benzene in propionaldehyde [Patrick and Burton, 1954] it was pointed out that propionaldehyde was most likely to have a triplet state lower than the triplet of benzene and " according to the energy transfer picture, benzene should not protect propionaldehyde. Any protection should be just in the opposite direction". Hydrogen was found by them to be a major product of the radiolysis of propionaldehyde [$G(H_2) = 1.2$, $G(CO) = 1.6$] and it is not clear which energy state of the aldehyde was considered responsible for its formation. They considered that the reduction of $G(H_2)$ with increasing electron fraction of benzene was due to the scavenging of H atoms by C_6H_6 and did not consider the possibility that the reduction might also be due to protection of propionaldehyde by it involving an energy transfer mechanism. Hydrogen was shown to be a minor product of the photolysis of propionaldehyde even at 238 mμ [$\phi_{CO} \frown 1$; $\phi_{H_2} \frown 0.1$; Blacet and Pitts, 1952]. The lowest singlet of propionaldehyde is at about 290 mμ and its triplet would be still lower [Rao, 1961; Reid, 1957]. So that, in the radiolysis of propionaldehyde [Patrick and Burton, 1954], hydrogen formation must have been due to excited states higher than the lowest triplet and from these states, then, energy transfer to benzene might have been possible.

The lowest singlet state of cyclohexanone is at about 290 mμ while the lowest singlet of benzene is at about 260 mμ and the triplet of the ketone might well be lower than the triplet of benzene [Rao, 1961; Reid,1957]. As has been pointed out already, these two states might not contribute

significantly to the hydrogen formation since sufficient energy for C-H bond rupture would not be available. Such arguement is consistent with the small photolytic production of H_2 from propionaldehyde [Blacet and Pitts, 1952] and with the absence of hydrogen amongst the photolytic products of cyclopentanone [Katayama et al, 1962].

Thus, if excited states of the cyclohexanone molecule are involved in the radiolytic production of hydrogen, they must be higher than the lowest singlet, and they may well be higher than the lowest states of benzene. Energy transfer from such excited states to benzene with consequent reduction of the hydrogen yield might thus be possible.

(ii) <u>2,3-Dimethyl-1,3-butadiene solutions.</u>

For the 2,3-dimethyl-1,3-butadiene solutions a satisfactory straight line plot could not be obtained (Fig IV.4). This may either be a result of inadequate precision of the $G(H_2)$ values obtained from these solutions or may be due to the inapplicability of such simple mechanisms (Mechanisms 2 and 5). The ionization potential of the diene (8.72 ev) [Price et al, 1959] is lower than that of cyclohexanone (9.14 ev) [Watanabe et al, 1962]. The lowest singlet of the diene is at 226 mμ [Rao, 1961] and the triplet is likely to be around 480mμ [Hammond et al, 1962]. So that, the lowest singlet of 2,3-dimethyl-1,3-butadiene is higher than the lowest singlet of the ketone, though the relative heights of the triplets cannot be judged since that of cyclohexanone is not known. Thus, both positive charge transfer and transfer of energy from relatively higher states from the ketone to the diene should be considered possible. However, on the basis of the present work, the role of the diene seems to be more complex than indicated by any one of the mechanisms given above. In the low concentration region ($\epsilon_s < 0.05$), the yield of hydrogen decreases much more rapidly from the 2,3-dimethyl-1,

FIGURE IV.4

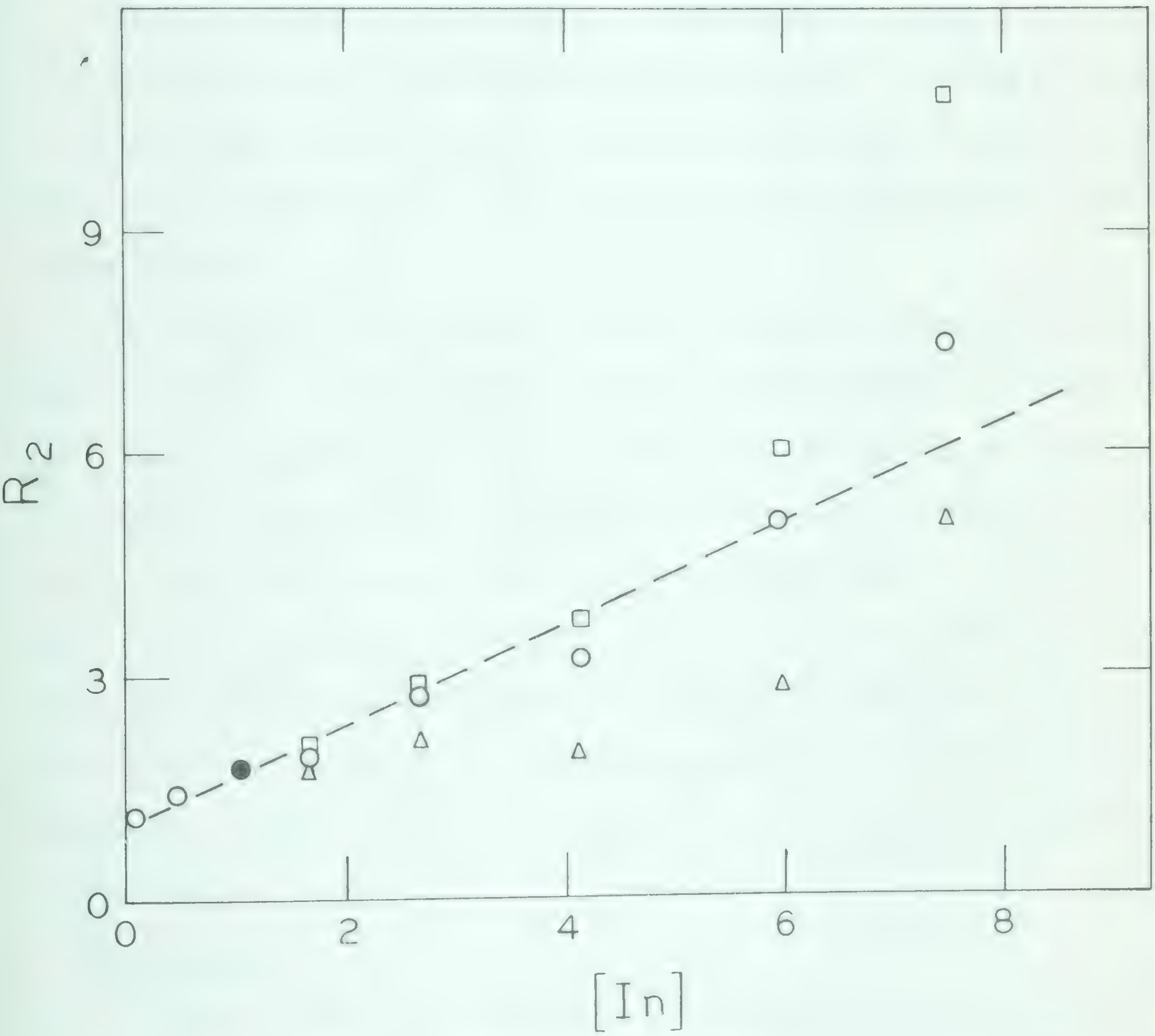
Kinetic Plot for Activation Transfer - Type Mechanism.

In = 2,3-Dimethyl-1,3- butadiene.

$$R_2 = (1 + v[In])\rho_2$$

Represents the point from which all other points were normalized. Triangles and squares are not shown for [In] $<$ 1.1 because they differed negligibly from the circles.

△	v =	0
○	v =	0.3
□	v =	1.0



R2
9
6
3
0
0
2
4
6
8
[In]

3-butadiene solutions than from the benzene solutions (Fig III.22), whereas in the higher concentration region the behaviour of the two inhibitors is similar. This further suggests that the role of the diene is more complex than that of benzene, which seems to be acting mainly by interfering with precursors of H_2 other than H atoms.

Certain activation transfer-type mechanisms would require a dependence of ρ on the dose rate. One such mechanism (Mechanism 6) is given in Appendix C. The present work was not extended to a study of the effect of dose rate on the solutions of cyclohexanone, so the applicability of such mechanisms cannot be tested here.

To summarize, the radiolytic formation of hydrogen from cyclohexanone seems to involve complex processes. It has not been possible to establish the presence or absence of H atoms in the system. In so much as cyclohexenone is a product of radiolysis of cyclohexanone, formation of molecular hydrogen is one of the possibilities (which is covered by Mechanism 2). However, since $G(H_2) = 0.76 > G(\text{cyclohexenone}) = 0.4$, if there is any molecular hydrogen formed at all, hydrogen must also be formed by other processes. The role of benzene in reducing the yield of hydrogen appears to involve interference with precursors of hydrogen, other than hydrogen atoms. The role of the diene is more complex.

2. Cyclohexanol.

It is postulated that cyclohexanol is formed from the reactions of the radical $(C_6H_{11}O)\cdot$ e.g. by hydrogen abstraction,

$$(C_6H_{11}O)\cdot + C_6H_{10}O \longrightarrow C_6H_{11}OH + (C_6H_9O)\cdot \qquad \text{(IV.38)}$$

and by disproportionation,

$$2(C_6H_{11}O)\cdot \longrightarrow C_6H_{11}OH + C_6H_{10}O \qquad \text{(IV.39)}$$

$$(C_6H_{11}O)\cdot + (C_6H_9O)\cdot \longrightarrow C_6H_{11}OH + C_6H_8O \quad \text{------------} \quad (IV.40)$$

$$\longrightarrow 2C_6H_{10}O \quad \text{----------------------} \quad (IV.41)$$

The radical $(C_6H_{11}O)\cdot$ may be formed in several different ways as follows.

a. $$C_6H_{10}O \rightsquigarrow C_6H_{10}O^+ + e^- \quad \text{----------------------} \quad (IV.42)$$

$$C_6H_{10}O + e^- \longrightarrow C_6H_{10}O^- \quad \text{------------------------------} \quad (IV.43)$$

$$C_6H_{10}O^+ + C_6H_{10}O^- \longrightarrow (C_6H_{11}O)\cdot + (C_6H_9O)\cdot \quad \text{-------------} \quad (IV.44)$$

b. $$C_6H_{10}O \rightsquigarrow (C_6H_9O)\cdot + H \quad \text{--------------------------------} \quad (IV.45)$$

$$C_6H_{10}O + H \longrightarrow C_6H_{11}O \quad \text{--------------------------------} \quad (IV.46)$$

$$\longrightarrow H_2 + (C_6H_9O)\cdot \quad \text{------------------------} \quad (IV.47)$$

The formation of H atoms in radiolytic systems and their addition to ketones has been postulated by various workers [e.g. Hardwick, 1962; Strong and Burr, 1959]. An experimental distinction between the reaction sequences (IV.42 - IV.44) and (IV.45 - IV.46) is difficult to make [Rao et al, 1962]. In the present work the extent of formation and participation of hydrogen atoms, if any, in the formation of radiolytic H_2 from cyclohexanone could not be determined, as has been discussed already. It may be mentioned that the reaction IV.45 may occur in more steps than one, e.g. the reaction sequence (IV.48 - IV.50) [Williams, 1962].

$$C_6H_{10}O \rightsquigarrow C_6H_{10}O^+ + e^- \quad \text{-----} \quad (IV.48)$$

$$C_6H_{10}O^+ + C_6H_{10}O \longrightarrow C_6H_{11}O^+ + (C_6H_9O). \quad \text{-----} \quad (IV.49)$$

$$C_6H_{11}O^+ + e^- \longrightarrow C_6H_{10}O + H \quad \text{-----} \quad (IV.50)$$

c. $$C_6H_{10}O \rightsquigarrow C_6H_{10}O^* \quad \text{-----} \quad (IV.51)$$

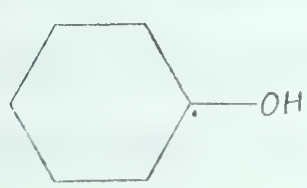
$$C_6H_{10}O^* + C_6H_{10}O \longrightarrow (C_6H_{11}O). + (C_6H_9O). \quad \text{-----} \quad (IV.52)$$

Hydrogen abstraction by a photoexcited carbonyl group ($n \rightarrow \pi^*$) is considered responsible for the formation of pinacols in the photolysis of solutions of ketones [e.g. Pitts et al, 1962; Porter and Wilkinson, 1961]. The photoexcited carbonyl group is also reported to abstract hydrogen from saturated hydrocarbons e.g. photolysis of acetone in cyclohexane gives isopropanol and pinacol along with other products [Yang and Yang, 1958]. A reaction of this type has also been postulated by Burr and Strong to explain the formation of benzpinacol in the radiolysis of solutions of benzophenone in 2-propanol [Burr and Strong, 1959].

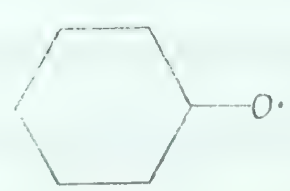
Structure of $(C_6H_{11}O)$.

It is interesting to very briefly speculate about some of the possible structures of $(C_6H_{11}O)$. which may be present in the system. It might have the following structures

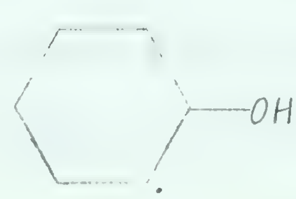
F.1



F.2



F.3



Radical F.1 would be important if $(C_6H_{11}O)\cdot$ is being formed by the reaction IV.52. Both, F.1 and F.2 may be important if $(C_6H_{11}O)\cdot$ is being formed by the other reactions. Radical F.3 might be important if the enol form of the ketone is important in radiolysis [Hardwick, 1962; Gero, 1954]. All the three can give cyclohexanol by hydrogen abstraction.

The radiolytic yield of cyclohexanol is shown in Figure III.14. The precision of the values does not allow any conclusions to be drawn about the variation of the yield with dose and the apparent increase with dose may not be real.

The yield of cyclohexanol is decreased to zero by 2,3-dimethyl-1, 3-butadiene at very low concentrations (Fig III.26). The diene is a good radical scavenger [Brown and James, 1962; Rajbenbach and Szwarc, 1959] and it probably inhibits the yield of cyclohexanol by scavenging $(C_6H_{11}O)\cdot$ radicals. The action of the diene is thus consistent with the postulated free radical mechanisms for the formation of cyclohexanol. The consumption of the diene which accompanys the reduction of the yields of cyclohexanol and the dimers (Fig III.38) further supports the role of the diene as a free radical scavenger in the system. However, the possibility that the diene might be acting by a selective quenching of the excited species of the ketone cannot be ruled out.

The effect of benzene on the yield of cyclohexanol is shown in Figure III.26, and its yield seems to decrease linearly with the increasing electron fraction of benzene. The precision of these values is not likely to be much better than the ones in Figure III.14, so that the linear decrease in Figure III.26 might not be real. Hence it cannot be said whether the formation of cyclohexanol is subject to inhibition by benzene or not though it seems certain that there is no radiosensitization. Benzene is a poor

radical scavenger [Levy and Szwarc, 1954] so that the effect of benzene is not inconsistent with the postulated free radical mechanism for the formation of cyclohexanol.

3. Cyclohexenone.

The following two modes of the formation of cyclohexenone, in the radiolysis of cyclohexanone, are postulated,

$$C_6H_{10}O \rightsquigarrow C_6H_8O + H_2 \quad \text{(IV.53)}$$

$$(C_6H_9O)\cdot + R\cdot \longrightarrow C_6H_8O + RH \quad \text{(IV.54)}$$

where R· is another free radical. In as much as the G value of cyclohexenone (o.4) is lower than the G value of hydrogen (0.76), the formation of cyclohexenone could be due to reaction (IV.53) above. Unfortunately, the extent of the contribution, if any, of this reaction to the yield of hydrogen in the present system is not known as discussed earlier. The importance of such reaction in other radiolytic systems has been a subject of much discussion [e.g. Hardwick, 1962; Dyne and Jenkinson, 1962; Burr, 1961]. However, since radical $(C_6H_9O)\cdot$ is probably formed in the system, reaction (IV.54) may be contributing to the yield of cyclohexenone to a significant extent.

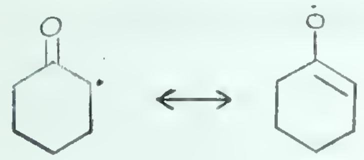
The radical $(C_6H_9O)\cdot$ might be formed by reactions (IV.38, IV.44, IV.45, IV.47, IV.49 and IV.52) as well as by the reaction (IV.55).

$$C_6H_{11}O^+ + e^- \longrightarrow (C_6H_9O)\cdot + H_2 \quad \text{(IV.55)}$$

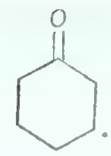
Structure of $(C_6H_9O)\cdot$

It is interesting to very briefly speculate about the possible structures of $(C_6H_9O)\cdot$ which may be formed by the above mentioned

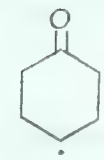
reactions, e.g. F.4 to F.6.



F.4



F.5



F.6

All the three could give cyclohexenone by disproportionation; F.4 could give only 2-cyclohexenone, F.6 could give only 3-cyclohexenone and F.5 could give both.

The yield of cyclohexenone decreases with increasing dose (Fig III.12), and this can be tentatively explained by the attack of free radicals, formed in the system, upon it.

$$R\cdot + C_6H_8O \longrightarrow (RC_6H_8O)\cdot \longrightarrow \text{Products} \text{-------------------} \quad (IV.56)$$

It has been shown [Rajbenbach and Szwarc, 1959] that conjugated dienes are much better radical scavengers than the isolated dienes. A similar difference is likely to be exhibited by 2- and 3- cyclohexenones and 2-cyclohexenone would likely disappear faster by reaction IV.56 due to its conjugate double bonds.

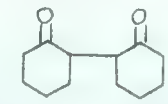
The effect of inhibitors on the radiolytic formation of cyclohexenone could not be determined because of analytical difficulties.

4. C_{12} products.

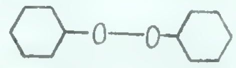
It is postulated that the C_{12} products are formed by combination reactions involving free radicals. Half of the dimer yield appears to be accounted for by 2,2'-diketodicyclohexyl (G values from the Silicone grease column; total dimer = 1.53; 2,2'-diketodicyclohexyl = 0.79) which suggests that the  = 0 radical is involved in the formation of the dimers (see F.4). Other $(C_6H_9O)\cdot$ radicals (F.5, F.6) and the $(C_6H_{11}O)\cdot$

radicals (F.1 - F.3) might also be involved.

The formation of 2,2' - diketodicyclohexyl could be from F.4 only,

2 F.4 $\longrightarrow$  ------------------ (IV.57)

It seems that reactions of the type IV.58 which would give peroxides

2 F.4 $\longrightarrow$  ------------------- (IV.58)

are probably not very important [G (peroxides) $\leqslant$ 0.3]. It must be added that this value refers to two high dose samples [$\sim$ 2-5(10^{20}ev/ml)] and may not be indicative of the yield of peroxides at lower doses where no meaningful measurement could be made.

The yield of total dimer decreases with increasing dose. This is attributable to secondary reactions.

Addition of 2,3-dimethyl-1,3-butadiene reduces the radiolytic yield of the dimer to zero at very low electron fraction of the diene (Fig III.35). This behaviour of the diene can be attributed to its radical scavenging action [Rajbenback and Szwarc, 1959; Brown and James, 1962] and is consistent with the postulated role of free radicals in the radiolytic formation of the dimers in cyclohexanone.

The effect of oxygen on the radiolytic formation of the dimers is very similar to that of 2,3-dimethyl-1,3-butadiene. Oxygen is known to act as a radical scavenger [Schuler, 1958] and its action here is consistent with the postulated formation of the dimers via free radical reactions.

The effect of benzene on the radiolytic formation of the total dimer is shown in Figure III.35, and is seen to be in sharp contrast to the effect of 2,3-dimethyl-1,3-butadiene (Fig III.35). Benzene is a poor radical scavenger [Levy and Szwarc, 1954] and the effect of benzene is not inconsistent with the postulated free radicals mechanisms for the formation of the dimers.

Benzene is probably protecting the ketone by activation transfer processes, thus inhibiting the formation of the free radicals responsible for dimer formation.

C. Products Involving C-C Bond Rupture.

The formation of the major products, i.e. 5-hexenal, CO and 1-pentene, and some of the minor products, e.g. ethylene, propylene and cyclopropane, can be understood in terms of reactions of diradicals formed by the opening of the cyclohexanone ring.

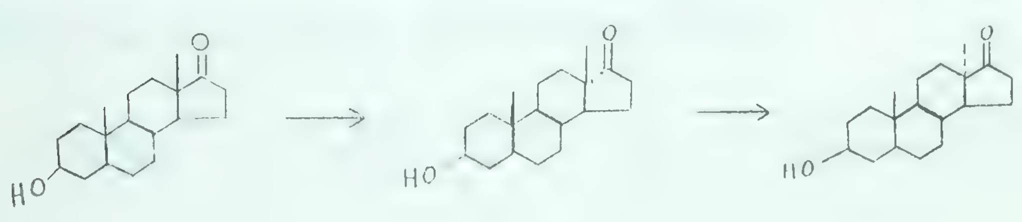
1. Evidence for diradicals.

The intermediate formation of diradicals has been invoked to explain the formation of photolytic products from cyclohexanone and other cyclic ketones by various workers [e.g. Blacet and Miller, 1957; Kharasch et al, 1953]. Srinivasan studied the photolysis of various cyclic ketones [Srinivasan, 1959], and suggested that the photolytic formation of 4-pentenal, 5-hexenal, 5-heptenal and 6-heptenal from cyclopentanone, cyclohexanone, 2-methylcyclohexanone and cycloheptanone respectively did not involve the intermediate formation of diradicals. More recently he has suggested that the intermediate formation of diradicals to explain the formation of CO and cyclobutane from cyclopentanone should also be discarded in favour of concerted mechanisms "until positive evidence for the diradical hypothesis is discovered" [Srinivasan,1961].

However, the evidence presented by Srinivasan does not establish the absence of diradicals and as he has himself pointed out, such species with life time less than $\sim 10^{-8}$ sec would have escaped detection in his system [Srinivasan, 1961]. Moreover, he has relied rather heavily on the effect of oxygen on the photolyses and the validity of his results is

questionable. For example, he found that the addition of oxygen increased the photolytic yield of 5-hexenal in the photolysis of cyclohexanone [Srinivasan, 1959]. In the present work, it has been found that the sample to which oxygen had been added, but which was not irradiated, gave a broad peak at the same place where 5-hexenal peak appears on gas chromatographic analysis (Ucon column). Srinivasan has not reported any dark reaction [Srinivasan, 1959]. He did his 5-hexenal analysis on a di-isodecylphthalate column whose overall behaviour is similar to that of the Ucon column [Dugle, 1962]. Such an effect of oxygen might also be occurring with other cyclic ketones and his results as well as the conclusions from photolyses of samples with added oxygen might be erroneous. He also seems to have overlooked the evidence obtained by other workers which supports the diradical hypothesis in photolyses of cyclic ketones, which follows.

Flowers and Frey studied the photolyses of cyclobutanone and cyclopentanone in the presence of excess of ethylene [Flowers and Frey,1960]. They found the presence of C_5 hydrocarbon products in the case of cyclobutanone and C_6 hydrocarbon products in the case of cyclopentanone. They explained their results on the assumption of the presence of trimethylene and tetramethylene diradicals as intermediates from the photolyses of the two cyclic ketones. Another example is provided by the photolytic conversion of androsterone to lumiandrosterone which must involve a diradical as an intermediate, formed by cleavage of one of the C-C bonds to the carbonyl group as follows [Mayo, 1960].



-----------(IV.59)

In the present system it has not been possible to establish the presence or absence of either the diradicals or the concerted mechanisms. However, the diradical hypothesis is consistent with the results obtained and will be used in the following treatment.

2. Speculation about the activated species involved.

The effect of benzene on the formation of the radiolysis products of cyclohexanone, seems to provide a key to the understanding of the underlying mechanisms. The effect of benzene on the formation of hydrogen and of the more important products involving ring rupture is summarized in Table IV.4 below.

TABLE IV.4

Effect of Benzene on the Radiolysis of Cyclohexanone.

Figure	Product	Yield, in Presence of Benzene	Role of Benzene
III.22	H_2	Decreased	Inhibition
III.22	C_2H_4	Unchanged	Merely Diluent
III.22 & III.26	CO & C_5 Hydrocarbons	Increased Slightly	Slight Radio-sensitization.
III.31	5-Hexenal	Increased Markedly	Marked Radio-sensitization.

This summary (Table IV.4)suggests that:

a. radiolytic hydrogen might arise from a group of excited states, which will be designated by $C_6H_{10}O^1$, such that benzene can interact with them to reduce the yield of H_2 by reaction IV.60,

$$C_6H_{10}O^1 + C_6H_6 \longrightarrow P_1 + P_2 \qquad \text{(IV.60)}$$

where P_1 and P_2 are products other than H_2 (see section B.1 above);

b. radiolytic formation of ethylene probably arises from another group of excited states ($C_6H_{10}O^2$) such that the reactions IV.61 - IV.63 occur;

$$C_6H_{10}O^2 \longrightarrow \dot{C}H_2(CH_2)_4\dot{C}O^{**} \quad \text{------------------------} \quad (IV.61)$$

$$\dot{C}H_2(CH_2)_4\dot{C}O^{**} \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}H_2^{*} + CO \quad \text{--------------------} \quad (IV.62)$$

$$\dot{C}H_2(CH_2)_3\dot{C}H_2^{*} \longrightarrow C_2H_4 + \dot{C}H_2CH_2\dot{C}H_2 \quad \text{-------------------} \quad (IV.63)$$

c. radiolytic formation of CO and 1-pentene [G(1-pentene) $\simeq$ 90% $\sum$G(C_5 products)]seems to arise from a group of excited states ($C_6H_{10}O^3$) such that the reactions IV.64 - IV.68 occur,

$$C_6H_{10}O^3 \longrightarrow \dot{C}H_2(CH_2)_4\dot{C}O^{*} \quad \text{--------------------------} \quad (IV.64)$$

$$\dot{C}H_2(CH_2)_4\dot{C}O^{*} \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}H_2 + CO \quad \text{--------------------} \quad (IV.65)$$

$$\dot{C}H_2(CH_2)_3\dot{C}H_2 \longrightarrow CH_2 = CHCH_2CH_2CH_3 \quad \text{--------------------} \quad (IV.66)$$

$$\longrightarrow \overline{CH_2CH_2CH_2CH_2CH_2} \quad \text{------------------------} \quad (IV.67)$$

$$C_6H_6^{*} + C_6H_{10}O \longrightarrow C_6H_{10}O^3 + C_6H_6 \quad \text{----------------------} \quad (IV.68)$$

where $C_6H_6^{*}$ is a group of activated species which can transfer activation to cyclohexanone, and which are produced by direct absorption of energy by benzene and perhaps also by reaction IV.60;

d. radiolytic formation of 5-hexenal probably arises from another group of excited states ($C_6H_{10}O^4$) such that the reactions IV.69 - IV.72 occur.

$$C_6H_{10}O^4 \longrightarrow \dot{C}H_2(CH_2)_4\dot{C}O \quad \text{------------------------} \quad (IV.69)$$

$$\dot{C}H_2(CH_2)_4\dot{C}O \longrightarrow CH_2 = CH\ CH_2CH_2CH_2CHO \quad \text{----------------} \quad (IV.70)$$

$$\longrightarrow \overline{CH_2(CH_2)_4CO} \quad \text{--------------------------} \quad (IV.71)$$

$$C_6H_6^* + C_6H_{10}O \longrightarrow C_6H_6 + C_6H_{10}O^4 \quad \text{--------------------} \quad (IV.72)$$

It would seem that the levels of excitation of the species follow the order $C_6H_{10}O^1 > C_6H_{10}O^2 > C_6H_{10}O^3 > C_6H_{10}O^4$. Inhibition of hydrogen and lack of inhibition of other products, by benzene, is consistent with the placement of $C_6H_{10}O^1$ at the head of this list, and increasing radiosensitization by benzene as one goes from $C_6H_{10}O^2$ to $C_6H_{10}O^4$ supports the remainder. Additional support is provided by the following consideration.

The bond dissociation energy for the C-C bond in acetone is = 72 kcal/mole [Cottrell, 1958]. To a first approximation, then, the reaction IV.73 would require

$$C_6H_{10}O \longrightarrow \dot{C}H_2(CH_2)_4\dot{C}O \quad \text{--------------------------} \quad (IV.73)$$

$\backsim$72 kcal/mole. The bond dissociation energy for the C-C bond in the acetyl radical is $\backsim$ 17 kcal/mole [Cottrell, 1958], so that reaction IV.74, to a first approximation, would require $\backsim$ 17 kcal/mole.

$$\dot{C}H_2(CH_2)_4\dot{C}O \longrightarrow \dot{C}H_2(CH_2)_3\dot{C}H_2 + CO \quad \text{--------------------} \quad (IV.74)$$

The energy required for reaction IV.75 is

$$CH_3CH_2\dot{C}H_2 \longrightarrow CH_3 + C_2H_4 \quad \text{------------------------} \quad (IV.75)$$

$\backsim$22 kcal/mole [Freeman, 1955] so that the energy required for reaction IV.76

$$\dot{C}H_2(CH_2)_3\dot{C}H_2 \longrightarrow C_2H_4 + \dot{C}H_2CH_2\dot{C}H_2 \quad \text{-----------------} \quad (IV.76)$$

may be $\backsim$ 22 kcal/mole, to a first approximation.

Thus the total minimum excitation energies for the species are roughly: $C_6H_{10}O^4 \sim$ 70 kcal/mole; $C_6H_{10}O^3 \sim$ 90 kcal/mole; $C_6H_{10}O^2 \sim$ 110 kcal/mole. The inhibition and radiosensitization might also be dependent upon the life times of the species involved. Other things being equal, a longer lived species would be more likely to undergo activation transfer processes than would one with a shorter life time.

Before proceeding to the consideration of individual products and the effect of other inhibitors upon them, it may be pointed out that the formation of CO, 1-pentene and 5-hexenal from energy states higher than $C_6H_{10}O^3$ and $C_6H_{10}O^4$, which might be subject to inhibition, such that radiosensitization $>$ inhibition ≥ 0, cannot be ruled out.

3. Individual products.

a. 5-Hexenal.

It is suggested that 5-hexenal arises from reaction IV.70, by intramolecular disproportionation of the pentamethylene acyl diradical. Marked radiosensitization of 5-hexenal by benzene is evident from Figure III.31. In the pure ketone, the yield of 5-hexenal decreases with increasing dose (Fig III.12) which may be attributed to secondary reactions. Thus, in the benzene solutions (Fig III.31), part of the initial increase in the yield of 5-hexenal may be due to partial inhibition of secondary reactions. A quantitative estimate of the extent of inhibition of these secondary reactions is not possible and thus a G_{ex} dashed line could not be drawn in Figure III.31. However, even if it were drawn from G_i (solid circle, Figure III.31.A), the radiosensitization would still be evident.

The effect of 2,3-dimethyl-1,3-butadiene on the radiolytic formation of 5-hexenal (Fig III.31) is in sharp contrast to that of benzene. The

sharp reduction of the yield of 5-hexenal (~50%) by the diene at very low concentrations ($\epsilon_s < 5 \times 10^{-3}$) might be due to scavenging of the pentamethylene acyl diradicals.

$$\dot{C}H_2(CH_2)_4\dot{C}O \ + \ C_6H_{10} \longrightarrow \text{Products} \quad \text{------------------------} \quad (IV.77)$$

If these diradicals have a long enough life time such that they are scavangeable at such low concentrations of the diene, it would seem that the diradicals must be in triplet states otherwise they would be expected to react more rapidly intramolecularly. On the other hand, the slow decrease in the yield of the rest of 5-hexenal (<50%) may be due to the scavenging of singlet state diradicals, which would be expected to have shorter life times. Magee has pointed out that up to 75% of the excited molecules formed subsequent to ion electron recombination may be in their triplet states [Magee, 1960]. The effect of added oxygen (Table III.8) is very similar to that of the diene and may be understood similarly. It is also possible that oxygen and the diene may be acting by some activation transfer processes, e.g. selective quenching of excited species of the ketone. Oxygen [Sester et al, 1962] and dienes [Hammond and Leermakers, 1962] are known to be efficient quenchers of triplet states.

b. Carbon monoxide.

Carbon monoxide may be formed by reactions IV.62 and IV.65.

The similar effect of benzene on the formation of CO and the C_5 hydrocarbons (Table IV.4; Figs. III.22 and III.26) suggests that most of the CO is arising from reaction IV.65. About 25% of it could be from reaction IV.62 [$G_i(C_2H_4) = 0.12$; $G_i(CO) = 0.48$] since benzene does not affect the yield of C_2H_4(Table IV.4; Fig. III.22).

The radiolytic formation of CO from cyclohexanone is decreased slowly by 2,3-dimethyl butadiene (Fig III.22). The effect of the diene is thus

in constrast to that of benzene.

c. 1-Pentene

Formation of both CO and 1-pentene according to reactions IV.65 and IV.66 would require that the inhibitors should affect the yields of these two products similarly. This is true for benzene which radiosensitizes the formation of both CO and 1-pentene (Figs III.22 and III.26). The yield of 1-pentene could not be measured from these solutions due to analytical difficulties and the conclusions here are based on the combined yield of the C_5 open chain hydrocarbon products [G(1-pentene) $\simeq$ 90% G(C_5 open chain hydrocarbon products) in pure cyclohexanone].

The effect of 2,3-dimethyl-1,3-butadiene on the yield of the C_5 hydrocarbon products could not be determined due to analytical difficulties. However, results from the two oxygen containing samples (Table III.8) show that the yield of the C_5 hydrocarbon products from them is lower than from the pure ketone. The effect of oxygen parallels that of 2,3-dimethyl - 1,3- -butadiene on the radiolytic yields of 5-hexenal and the dimers. It might therefore be assumed that the effect of the two inhibitors would be similar on the radiolytic production of the C_5 hydrocarbons as well.

d. Minor products.

(i) Ethylene is probably formed by reaction IV.63. Its yield seems to be unaffected by the two inhibitors used (C_6H_6, C_6H_{10}; Fig III.22).

(ii) Cyclopropane and propylene are presumably formed from the trimethylene diradical (reaction IV.63) as follows.

$$\dot{C}H_2CH_2\dot{C}H_2 \longrightarrow \overline{CH_2CH_2CH_2} \quad \text{--------------------------} \quad (IV.78)$$

$$\longrightarrow CH_3CH = CH_2 \quad \text{--------------------------} \quad (IV.79)$$

There is considerable evidence [Bawn and Hunter, 1938; Flowers and Frey, 1960] that the trimethylene diradical is involved in the formation of these two hydrocarbons in the reaction of Br $CH_2CH_2CH_2Br$ with sodium and in the photolysis of cyclobutanone. The effect of inhibitors on the radiolytic formation of cyclopropane and propylene could not be determined due to experimental difficulties.

(iii) The yield of cyclopentane is very small. It probably arises from reaction IV.67. The effect of benzene on its yield is shown in Fig III.26.

(iv) The data obtained in the present work do not allow any conclusions to be drawn about the mode of formation of the other minor products i.e. acetylene, ethane, methylacetylene, allene, propane, n-butane, 1-butene, butadiene, 2-pentene, and n-pentane. Further, it is difficult to decide to what extent the diradicals involved in the reactions given above would add on to other reactive species in the system to form C_{12} or smaller products. It may be pointed out that none of the four unidentified dimers (D.1-D.4) was found to be radiosensitized by benzene. This might be taken to mean that C_6 diradicals are not involved to any significant extent in their formation.

D. Miscellaneous.

1. Polymer.

The yield of polymer is shown in Figure III.19 and apart from the large experimental error in the estimations, which is apparent in the Figure, it is not certain whether the linear extrapolation to get the value at zero dose is valid. The yield of polymer does seem to increase with dose which is not inconsistent with the decrease in the G values of dimers and of the unsaturated products.

Polymer formation has been reported in the photolysis of cyclohexanone [Benson and Kistiakowsky, 1942; Blacet and Miller, 1957] and has been attributed to the hydrocarbon diradicals by Blacet and Miller. It is possible that the C_6 diradicals may also be participating in the polymer formation in his system. In the present case the polymer is found to contain large percentage of oxygen (Table III.7). The C_6 and other diradicals, the monoradicals [$(C_6H_9O)\cdot$ and $(C_6H_{11}O)\cdot$] and the ions might therefore be involved in the formation of the polymer, in the present case.

The effect of the inhibitors on the formation of the polymer could not be determined due to analytical difficulties.

2. Further comments on the role of 2,3-dimethyl-1,3-butadiene in the radiolysis of the ketone.

The diene seems to have a dual role. In the low concentration region ($\epsilon_s < 3 \times 10^{-3}$), it completely inhibits the formation of cyclohexanol and the dimers and reduces the yield of 5-hexenal substantially [Figs. III.26, III.35 and III.31 respectively). It has been suggested in the preceding discussion that the diene might be acting mainly as a radical scavenger in these instances. The attack of a free radical on the diene would give an allylic type radical (F.7).

$$R\cdot + CH_2 = C(CH_3) - C(CH_3) = CH_2 \longrightarrow \underbrace{RCH_2 - \dot{C}(CH_3) - C(CH_3) = CH_2}_{F.7} \qquad (IV.80)$$

The radical F.7 could then: (a) add on to another free radical to form a product greater than C_{12}; (b) abstract hydrogen and give a C_{12} product or (c) add on to another molecule of 2,3-dimethly-1,3-butadiene to initiate a chain reaction.

The last possibility would require an increasing value of

G(consumption) of the diene with its increasing electron fraction in the solutions radiolysed. Further, the value of the ratio of the diene units to the cyclohexanone units in the polymer is ~ 1 which is consistent with the absence of a chain reaction. The second possibility would require the formation of C_{12} products of the type $C_{12}H_{20}O$. However, such products were not observed in solutions with $\epsilon_s \sim 2 \times 10^{-3}$ where the yields of the dimers and cyclohexanol had been reduced to zero.

This leaves the first possibility that the radical F.7 combines with another free radical to give a product greater than C_{12}. The formation of the polymer (G = 7.3, Table III.10) with $\sim$1:1 ratio of diene units to cyclohexanone units in it is consistent with this consideration.

An additional process involving the diene is evident at concentrations with $\epsilon_s \geqslant 1 \times 10^{-2}$, with a maximum at $\epsilon_s \sim 0.1$. This involves a sharp increase in the yield of the main dimer of 2,3 - dimethyl - 1,3- -butadiene and also a sharp increase in the total yield of the dimers that contain the diene unit (Fig III.37). This behaviour of the diene might involve direct addition of excited cyclohexanone molecules to the diene.

$$C_6H_{10}O^* + C_6H_{10} \longrightarrow C_{12}H_{20}O \quad \text{------------------------} \quad (IV.81)$$

This addition may either involve reaction with the conjugated double bond system of the diene (1:4 addition) or it may involve a reaction with only one of the double bonds [Kharasch type addition; see Mayo, 1960]. This would, however, not lead to the dimerization of the diene itself. The rapid initial increase in the yield of the dimer of 2,3-dimethyl-1,3- -butadiene could arise from any of the types of inhibition reactions mentioned earlier.

3. <u>The value of G (radicals).</u>

The value of G(consumption) of 2,3-dimethyl-1,3-butadiene in the

maximally inhibited system in the low concentration region ($\epsilon_s < 5 \times 10^{-3}$, Fig III.38) is about 4. Assuming that the polymer formation from the ketone itself is insignificant in the presence of the diene, then on the basis of arguments advanced in section 2 above G(radicals) may be taken as ~ 4. If, however, the polymer formation from the ketone remains significant, then this value may be as low as ~ 2.

The average value of G(peroxides) from the two oxygen containing samples (Table III.8) is about 3. Since a peroxide molecule may represent either one or two molecules of ketone, a value of G(radicals) ~ 3 may be too low. The yield of a $C_6H_8O_2$ type product (other than peroxide) was estimated to be $G \simeq 1$ (section III.B.2.d.). Thus the value of G(radicals) from oxygen containing samples would be $\gtrsim 4$.

On the basis of the values of G(radicals) $\lesssim 4$ from the diene solutions and G(radicals) $\gtrsim 4$ from the oxygen solutions, it appears that the value of G(radicals) is about 4.

An indication of the value of G(scavangeable radicals) in pure ketone is given by the expression IV.82.

$$
\begin{aligned}
G(\text{scavengeable radicals}) &\simeq \\
&\simeq 2\,G(C_6H_{11}OH) + 2G(C_6H_8O) + 0.6\,G(\text{5-hexenal}) + \\
&+ G(\text{polymer}) + 2G(\text{dimers}) \\
&= (1.0 \pm 0.4) + (0.8 \pm 0.4) + (0.5 \pm 0.1) + (1.8 \pm 0.3) + \\
&+ (2.3 \pm 0.9) \qquad \text{------------------------} \quad (IV.82)
\end{aligned}
$$

i.e. G(scavengeable radicals) $\simeq 6 \pm 2$

This value is subject to some uncertainties, e.g. (i) C_6H_8O may be formed molecularly which would make this value too high;(ii) the polymer may not be a primary product which would also make this value too high;

(iii) the disproportionation reaction, IV.83, may be occurring which would

$$(C_6H_{11}O)\cdot + (C_6H_9O)\cdot \longrightarrow 2\, C_6H_{10}O \quad \text{---------------------} \quad (IV.83)$$

make this value too low.

In view of the uncertainties in the measured and predicted values of G(radicals) no conclusion about the apparent discrepancy between them is warranted.

E. Concluding Remarks.

The amount of radiolytic ring cleavage has been found to be greater in cyclohexanone than that found in cyclohexane by other workers (Table IV.3). A point of interest in this regard is the amount of regeneration of the substrate that might be taking place following the initial ring opening. Work with various isomers of optically active derivatives of cyclohexanone with an asymmetric carbon atom in the ring might provide useful information on this point. Work with such compounds might also provide useful information about the mechanisms of formation of various other products, since, in general, any product whose formation involves a free radical site at the asymmetric carbon atom would show considerably reduced optical rotation.

Activation transfer-type mechanisms seem to be favoured for the inhibition by benzene of the formation of hydrogen from cyclohexanone (section IV.B.1.b). Inhibition of hydrogen by 2,3-dimethyl-1,3-butadiene seems to be more complex. One mechanism was considered which predicted dose rate dependence for the inhibition of hydrogen, but which could not be tested with the present data (Mechanism 6). Studies of inhibited systems as a function of dose rate might be helpful in deciding about the applicability of such a mechanism.

Activation transfer type processes also seem to be involved in the inhibition of the dimers and sensitization of some other products (CO, 1-pentene and 5-hexenal) by benzene (sections IV.B.4 and IV.C.2). It might be interesting to compare this intermolecular effect of benzene with its intramolecular effect e.g. by a comparison of the radiolyses of (C_6H_6 + $C_6H_{10}O$) and C_6H_5 - C_6H_9O. Radiolysis of

the latter would be expected to have a low hydrogen yield but it might show, simultaneously, sensitized formation of CO and opening of the cyclohexanone ring.

Radiolytic data from the 2,3-dimethyl-1,3-butadiene solutions suggests that three important processes by which the diene might be acting are radical scavenging, activation transfer from the ketone and direct addition to excited cyclohexanone molecules. Radical scavenging seems to be important in the inhibition of cyclohexanol and dimer formation at very low diene concentrations (sections IV.B.2 and IV.B.4). At least two processes seem to be operative in H_2 inhibition by the diene as is evident from the rapid decrease in its yield at low diene concentrations and relatively slower decrease at the higher diene concentrations (Fig III.22). It is difficult to say whether one of these involves a scavenging process (Mechanism 1, etc) or whether both of these are activation transfer type processes (Mechanism 2, etc). The occurrence of activation transfer from the ketone to the diene is evident from the sensitized formation of the main dimer of the diene (section IV.D.2). Direct addition of the diene to excited cyclohexanone molecules is indicated by the formation of mixed dimers of the ketone and the diene at higher concentrations of the latter (section IV.D.2); these mixed dimers are absent at very low concentrations of the diene - in the region where the yields of cyclohexanol and the dimers are reduced to zero. Use of this inhibitor in the radiolysis of other ketones might provide further insight into its modes of action.

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APPENDIX A

Additional Scavenging - Type Mechanisms.

1. Mechanism 3.

$$C_6H_{10}O \xrightarrow{I_3} C_6H_{10}O^+ + e^- \quad (12)$$

$$C_6H_{10}O^+ + C_6H_{10}O \longrightarrow C_6H_{10}OH^+ + (C_6H_9O). \quad (13)$$

$$C_6H_{10}OH^+ + e^- \longrightarrow \eta \longrightarrow H_2 + P_1 \quad (14)$$

$$C_6H_{10}O^+ + In \longrightarrow C_6H_{10}O + In^+ \quad (15)$$

$$In^+ + e^- \longrightarrow In^* \quad (16)$$

$$In^* \longrightarrow \eta \longrightarrow H_2 + P_2 \quad (17)$$

$$In^* \longrightarrow In \quad (18)$$

Steady state treatment of this mechanism gives the following expression

$$\left(1 + y \frac{[In]}{[C_6H_{10}O]}\right) \mathcal{f}_3 = 1 + z \frac{[In]}{[C_6H_{10}O]}$$

where $y = \dfrac{k_{15}\ k_{17}}{k_{13}\ (k_{17} + k_{18})}$,

$z = \dfrac{k_{15}}{k_{13}}$,

and the other notations having neanings similar to those for Mechanisms 1 and 2.

2. Mechanism 4.

$$C_6H_{10}O \xrightarrow{I_4} C_6H_{10}O^+ + e^- \quad \text{------------------} \quad (19)$$

$$C_6H_{10}O^+ + C_6H_{10}O \longrightarrow C_6H_{10}OH^+ + (C_6H_9O). \quad \text{------------------} \quad (20)$$

$$e^- + C_6H_{10}O \longrightarrow C_6H_{10}O^- \quad \text{------------------------------} \quad (21)$$

$$C_6H_{10}OH^+ + C_6H_{10}O^- \longrightarrow \eta \longrightarrow H_2 + P_1 \quad \text{-----------------------} \quad (22)$$

$$\longrightarrow P_2 \quad \text{------------------------------} \quad (23)$$

$$e^- + In \longrightarrow In^- \quad \text{-----------------------------------} \quad (24)$$

$$C_6H_{10}OH^+ + In^- \longrightarrow P_3 \quad \text{-----------------------------------} \quad (25)$$

$$C_6H_{10}OH^+ + In^- \longrightarrow \eta \longrightarrow H_2 + P_4 \quad \text{-------------------------} \quad (26)$$

Steady state treatment of this mechanism gives the following expression

$$\left(1 + y \frac{[In]}{[C_6H_{10}O]}\right) f_4 = 1 + z \frac{[In]}{[C_6H_{10}O]}$$

$$\text{where } y = \frac{k_{24}\ k_{26}}{k_{21}\ (k_{25} + k_{26})},$$

$$z = \frac{k_{24}}{k_{21}}$$

and the other notations have meanings similar to those for Mechanisms 1 and 2.

APPENDIX B.

An Additional Activation Transfer - Type Mechanism.

Mechanism 5.

$$C_6H_{10}O \overset{I_5}{\rightsquigarrow} (C_6H_{10}O^+ \; + \; e^-) \text{ -------------------- } (27)$$

$$(C_6H_{10}O^+ \; + \; e^-) \longrightarrow \quad q \rightarrow H_2 + P_1 \text{ -------------------- } (28)$$

$$(C_6H_{10}O^+ \; + \; e^-) \; + \; In \rightarrow (C_6H_{10}O^+ \; + \; In^-) \text{ ---------------- } (29)$$

$$(C_6H_{10}O^+ \; + \; In^-) \longrightarrow \quad q \longrightarrow H_2 + P_2 \text{ -------------------- } (30)$$

$$(C_6H_{10}O^+ \; + \; In^-) \longrightarrow \quad C_6H_{10}O \; + \; In \text{ ------------------- } (31)$$

where $(C_6H_{10}O^+ \; + \; e^-)$ means that the electron does not escape the field of the parent ion and thus has no independent existence.

Steady state treatment of this mechanism gives the following expression.

$$\left|1 + v\,[In]\right| \rho_5 = 1 + u\,[In]$$

$$v = \frac{k_{29}\;k_{30}}{k_{28}(k_{30} + k_{31})},$$

$$u = \frac{k_{29}}{k_{28}},$$

and the other notations have meanings similar to those for Mechanisms 1 and 2.

APPENDIX C

A Mechanism That Predicts Dose Rate Dependence of the Inhibition.

Mechanism 6.

$$C_6H_{10}O \xrightarrow{I_6} C_6H_{10}O^+ + e^- \quad \text{------------------} \quad (32)$$

$$C_6H_{10}O^+ + C_6H_{10}O \longrightarrow C_6H_{10}OH^+ + (C_6H_9O). \quad \text{--------------} \quad (33)$$

$$C_6H_{10}OH^+ + e^- \longrightarrow \text{ч} \longrightarrow H_2 + P_1 \quad \text{--------------------} \quad (34)$$

$$In + e^- \longrightarrow In^- \quad \text{--------------------------------} \quad (35)$$

$$C_6H_{10}OH^+ + In^- \longrightarrow (C_6H_{11}O). + In \quad \text{----------------------} \quad (36)$$

Steady state treatment of this mechanism gives the following expression

$$\left(\frac{I_6}{d[H_2]/dt}\right) = \rho_6 = 1 + \left\{\frac{k_{35}\,[In]}{\dfrac{k_{33}[C_6H_{10}O] - 1}{k_{33}\,[C_6H_{10}O]}\; k_{34}\, I_6}\right\},$$

$$\text{i.e.} \quad (\rho_6 - 1)\left(1 - \frac{1}{k_{33}[C_6H_{10}O]}\right) = \frac{k_{35}\,[In]}{k_{34}\, I_6},$$

where the notations have meanings similar to those in Mechanisms 1 and 2.